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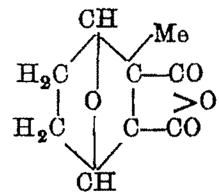
281		formula (I).	
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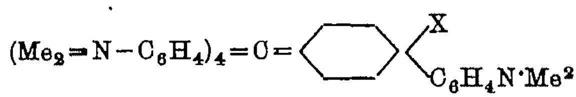
Read 

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Simple and Complex Metallic Salts of Thiosulphato-pentacyano-cobaltic Acid.

By Sailendra Nath Maulik.

The potassium salt of thiosulphato-pentacyano-cobaltic acid has been described by Rây (*J. Indian Chem. Soc.*, 1927, **5**, 325). The free acid was subsequently isolated and its alkali and alkaline earth salts were also studied (Rây and Maulik, *Z. anorg. Chem.*, 1931, **199**, 355). The present work was undertaken to study the preparation and properties of a number of other metallic and metal-ammonium salts.

The following list shows the compositions of the compounds prepared.

I. $BeO \cdot Be_2[(CN)_5 \cdot Co \cdot S_2O_3]\ 2H_2O$
II. $K_2Mn[(CN)_5 \cdot Co \cdot S_2O_3]\ 4H_2O$
III. $Mn_2[(CN)_5 \cdot Co \cdot S_2O_3]\ 6H_2O$
IV. $[Cu(NH_3)_4]_2[(CN)_5 \cdot Co \cdot S_2O_3]$
V. $[Cu(NH_3)_2]_2[(CN)_5Co \cdot S_2O_3]3H_2O$ and in the anhydrous state.
VI. $[Zn(NH_3)_4]_2[(CN)_5 \cdot Co \cdot S_2O_3]$
VII. $[Zn(NH_3)_2]_2[(CN)_5 \cdot Co \cdot S_2O_3]4H_2O$
VIII. $[Ni(NH_3)_5]_2[(CN)_5 \cdot Co \cdot S_2O_3]$
IX. $[Ni(NH_3)_2]_2[(CN)_5 \cdot Co \cdot S_2O_3]\ 6H_2O$
X. $Ag_4[(CN)_5 \cdot Co \cdot S_2O_3]$
XI. $Ag_4[(CN)_5 \cdot Co \cdot S_2O_3]\ 4\frac{1}{2}\ NH_3,\ 6\frac{1}{2}H_2O$.

Experimental.

Basic beryllium salt (I).—A freshly prepared solution of the free complex acid (Rây and Maulik, *loc. cit.*) was saturated with beryllium oxide; the solution was filtered and kept in vacuum over sulphuric acid. When the liquid was reduced to half its volume, it was filtered again and evaporated finally to dryness in a vacuum. The orange-red substance is very soluble in water. This property is characteristic of many beryllium salts. (Found: Be, 6·95; Co, 15·54; $BeO \cdot Be_2[(CN)_5 \cdot Co \cdot S_2O_3]\ 2H_2O$ requires Be, 7·1; Co, 15·5 per cent)

Manganese potassium salt (II).—Manganese chloride (2·5 g.) dissolved in the least quantity of water was added, drop by drop, with constant stirring to a cold saturated solution of 5 g. of the potassium salt (Râу, *loc. cit.*). The precipitate, formed, was filtered and washed with ice-cold water, then with cold dilute alcohol and finally with absolute alcohol. When dried in air, the substance formed a pale yellow crystalline powder. (Found: Co, 11·56; K, 15·45; Mn, 10·88. $MnK_2\,[(CN)_5\cdot Co\cdot S_2O_3]\,4H_2O$ requires Co, 11·66; K, 15·41; Mn, 10·90 per cent).

Manganese salt (III).—Calcium salt (2·5 g.) (Râу and Maulik, *loc. cit.*) was added to the solution of an excess of manganese chloride (25 g. in 15 c.c. water). The mixture containing the thick precipitate was carefully heated in the water-bath till it completely went into solution. This was then filtered and allowed to evaporate at the ordinary temperature in air. The crystals formed, were drained, washed at first with cold water, then with alcohol, and finally dried in air. (Found: Co, 11·47; Mn, 21·30. $Mn_2[(CN)_5\cdot Co\cdot S_2O_3]\,6H_2O$ requires Co, 11·37; Mn, 21·16 per cent).

Tetra- and di-ammonium copper salt (IV & V).— Calcium salt (5 g.) dissolved in the least quantity of cold water, was added to cold saturated solution of crystallised cupric chloride (5 g.) with constant stirring. The gelatinous precipitate, produced, was filtered through a Buchner funnel, and the mother liquor was drained as far as possible. The solid mass was then transferred to a small conical flask with about 25 c.c. of water. The flask was cooled in ice and ammonia gas was passed through the mixture. The substance gradually went into solution. On maintaining the current of ammonia gas for about 2 hours, blue crystals separated from the solution. These were purified by dissolving them in the least quantity of water and saturating the solution again with ammonia gas at a low temperature. The blue crystals, reprecipitated, were drained, washed with a cold saturated solution of ammonia, followed by ice-cold alcoholic ammonia. They were then dried over quick lime in an atmosphere of ammonia gas. (Found: Co, 10·52; Cu, 22·35; NH_3, 24·12. $[Cu(NH_3)_4]_2\,[(CN)_5\cdot Co\cdot S_2O_3]$ requires Co, 10·4; Cu, 22·38; NH_3, 24·15 per cent).

When the above compound was exposed to the atmospheric air, it lost ammonia and turned green. When the weight became constant it was analysed. (Found: Co, 10·78; Cu, 22·78; NH_3, 12·27.

$[Cu(NH_3)_2]_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]3H_2O$ requires Co, 10·75; Cu, 22·95; NH_3, 12·39 per cent).

When dried over quick lime, the green crystals lost their water of crystallisation. No loss of ammonia, however, occurred. (Found: Cu, 25·57; NH_3, 13·69. The anhydrous salt requires Cu, 25·47; NH_3, 13·74 per cent).

Tetra- and di-ammonium zinc salt (VI & VII).—A solution of calcium salt (5 g.) in about 20 c.c. of water was added with constant stirring to a solution of an equal weight of zinc chloride in 25 c.c. of water. The jelly-like mass, thus obtained, was drained as thoroughly as possible and then transferred to a small conical flask with a little water. This was treated with ammonia gas at low temperature till a clear solution was obtained. This was filtered, and the filtrate was cooled in ice and saturated with ammonia gas. The crystals, separated, were purified by dissolving them in water, and saturating the solution once again with ammonia gas. The pure crystals were filtered and washed with cold concentrated ammonia followed by alcoholic ammonia. These were dried over quick lime in an atmosphere of ammonia. (Found: Co, 10·31; NH_3, 23·92; Zn, 23·14. $[Zn(NH_3)_4]_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$ requires Co, 10·41; NH_3, 23·98; Zn, 22·93 per cent).

When the purified crystals were dried to constant weight in air, they lost ammonia and changed to the diammino compound. (Found: Co, 10·34; NH_3, 11·85; Zn, 22·84. $[Zn(NH_3)_2]_2$-$[(CN)_5{\cdot}Co{\cdot}S_2O_3]$ $4H_2O$ requires Co, 10·34; NH_3, 11·91; Zn, 22·77 per cent).

Penta- and di-ammonium nickel salts (VIII & IX).—A solution of calcium salt (5 g.) was added to a solution of an equal weight of nickel chloride crystals in the cold. The precipitate obtained was drained and treated with ammonia as described under the copper salt. The crystals separated were dissolved in dilute ammonia and reprecipitated from the solution by the passage of ammonia gas. The yellowish-green crystals, thus obtained, were dried over quick lime in an atmosphere of ammonia. (Found: Co, 9·18; Ni, 18·24; NH_3, 26·65. $[Ni(NH_3)_5]_2$ $[(CN)_5{\cdot}$-$Co{\cdot}S_2O_3]$ $3H_2O$ requires Co, 9·19; Ni, 18·28; NH_3, 26·46 per cent). The composition of this compound is rather unusual, as the nickel atom appears to have a co-ordination number of 5 with respect to ammonia. It may, however, be represented as $[Ni(NH_3)_5H_2O]_2$-$[(CN)_5{\cdot}Co{\cdot}S_2O_3]H_2O$.

When exposed to the atmosphere, the yellowish green crystals rapidly lost a part of its ammonia and turned green. (Found: Ni, 19·68; NH_3, 11·52. $[Ni(NH_3)_2]_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]\,6H_2O$ requires Ni, 19·75; NH_3, 11·44 per cent).

Silver salt (X).—A cold aqueous solution of the potassium salt (3 g.) was added drop by drop with constant stirring to an ice-cold solution of silver nitrate (5 g.). The precipitated silver salt was washed by decantation with water at 0° till free from soluble matter. It was then filtered at the pump, washed with cold alcohol and dried over sulphuric acid. The substance formed a light yellow powder. (Found: Ag, 59·1; Co, 8·04. $Ag_4[CN)_5{\cdot}Co{\cdot}S_2O_3]$ requires Ag, 58·94; Co, 80·5 per cent).

Silver ammonium salt (XI).—The freshly prepared silver compound was dissolved in concentrated ammonia in the cold, and the solution was saturated with ammonia gas at 0°. The crystals separated were drained, washed at first with cold alcoholic ammonia and then with ether. The compound is extremely unstable, and rapidly turns black due to decomposition. (Found: Ag, 46·83; Co, 6·31; NH_3, 8·41. $Ag_4[(CN)_5{\cdot}Co{\cdot}S_2O_3].4\frac{1}{2}NH_3, 6\frac{1}{2}H_2O$ requires Ag, 46·67 ; Co, 6·37 ; NH_3, 8·31 per cent).

The composition indicates that 8 silver atoms are associated with 9 ammonia molecules, showing that the co-ordination number for silver varies between 2 to 1 here.

The author wishes to express his grateful thanks to Prof. P. Rây for his kind interest in the work and the encouragement received from him.

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Nickel Salts as Light Filters.

By W. V. Bhagwat.

It is well known that the addition of nickel oxide makes a glass very suitable for the transmission of *ultraviolet* rays and cutting of visible and infra-red radiations. Coblentz (*Bureau of Standards*, 1911, No. 7, 658) examined nickel chloride in search of a substance which absorbs all the infra-red rays. Emerson, Coblentz and Lang (*ibid.*, 1918, No. 325, 658) determined the transmission of a one cm. layer of nickel sulphate $NiSO_4, 7H_2O$, nickel nitrate $Ni(NO_3)_2$ and nickel acetate $Ni(C_2H_3O_2)_2$, the concentration in all cases being 10 g. of salt in 100 c.c. of water. Their results are summarised in the following table.

λ = Wave-length in Å units. $\%T$ = Percentage transmission.

λ	6000	7000	8000	9000	10000	11000	12000	13000
$\%T$, $NiSO_4$	42	21	58	64	33	16	9	4·5
$\%T$, $Ni(NO_3)_2$	42	11	50	64	33	15	8	4
$\%T$, $Ni(C_2H_3O_2)_2$	25	10	35	46	23	10	4	2

They have plotted the transmission curves. They are of interest in showing a sharp absorption bend at $0·7\mu$ followed by complete opacity at $1·4\mu$ caused by the abosrption of water. None of these solutions were found to be as suitable as cupric chloride for absorbing infra-red. Solutions of nickel sulphate, potassium chromate and potassium permanganate are said to transmit the wave-length 6140-5760Å. Houstoun (*Proc. Roy. Soc. Edin.*, 1911, **31**, 538, 547) has also investigated the absorption of nickel salts in visible, infra-red and ultraviolet for some concentrations but has not discussed thier use as light filters.

The author has determined the absorption and percentage transmission of solutions of nickel chloride, nickel nitrate, nickel sulphate and nickel ammonium sulphate of various concentration. The method of measurement is the same as given in previous papers (Bhagwat and Dhar, *J. Phys. Chem.*, 1931, **35**, 2383) and the

concentration of nickel sulphate and nickel ammonium sulphate have been determined by estimating as sulphate.

Nickel Chloride.

λ = Wavelength in Å unit. M = Molar concentration. $\%T$ = Percentage transmission. e = Extinction coefficient.

$$\text{Normal solution} = N = \frac{\text{M. W. of nickel salt}}{2}.$$

(1) Concentration 4·63 N.

λ.	e.	%T.	λ.	e.	%T.
4000—4750	∞	0	5600	1·03	9·5
4800	2·0	1	5800	1·36	4·3
5000	1·04	9·1	6000	2·0	1
5200	0·77	16·9	6050	∞	0
5400	0·84	14·4	7000	...	...

(2) Concentration 4·63N.

λ.	e.	%T.	λ.	e.	%T
000—4400	∞	0	5400	0·46	34·7
4500	1·50	3·1	5600	0·600	25·2
4600	1·08	8·3	5800	0·88	13·2
4800	0·58	26·3	6000	1·38	4·1
5000	0·37	42·7	6200	2·0	1
5200	0·40	39·8	6320—7000	∞	0

(3) Concentration 0·926N.

λ.	e.	%T.	λ.	e.	%T.
4400	0·48	33·1	5800	0·27	53·7
4600	0·21	61·7	6000	0·36	43·4
4800	0·23	58·9	6200	0·57	26·9
5000	0·16	69·2	6400	0·77	16·9
5200	0·16	69·2	6600	0·87	13·4
5400	0·18	66·1	7000	0·92	12·1
5600	0·22	60·3			

Thus the limit of transmission for these salts are as follows.

Concentration.	Range of transmission.	Maximum %T.
9·26N	4750—6050Å	16·9
4·63	4400—6320	42·7
0·926	4000—7000	69·2

The results of absorption of nickel nitrate solutions of various concentrations have already been published. The limit of transmission for this salt are as given below.

Concentration.	Range of transmission.	Maximum %T.
4·16M	4400-6100 A°	7·9
2·08	4300-6400 A°	30·2
1·04	All visible	56·2
0·208	Do	91·2

It will be seen from these results that nickel chloride like cupric chloride absorbs highly at both the ends of visible spectrum. However it has got a very long range of transmission, even the most concentrated solution transmitting as long a region as 4750—6050Å. It will also be clear that nickel chloride differs from nickel nitrate in that it does not obey Beer's law of absorption.

Infra-red absorption for nickel nitrate hes been determined by Coblentz, Emerson and Lang (*loc. cit.*) for 10% solution. Assuming Beer's law, infra-red absorption for other concentrations examined by the author has been calculated.

Concentration 4·16M.				Concentration 2·08M.			
λ.	%T.	λ.	%T.	λ.	%T.	λ.	%T.
7000	0	11000	0	7000	0·04	11000	0·12
8000	0·67	12000	0	8000	8·30	12000	0·026
9000	3·93	13000	0	9000	10·2	13000	0
10000	0·037	14000	0	10000	1·99	14000	0

Nickel Sulphate.

(1) Concentration 5·28*N*.

λ.	ε.	%*T*.	λ.	ε.	%*T*.
6250	∞	0	5200	0·40	39·8
6200	2·35	0·44	5000	0·27	53·7
6000	1·65	2·2	4800	0·48	33·1
5800	1·85	9·1	4600	0·90	12·5
5600	0·65	22·3	4500	1·40	3·98
5400	0·50	31·6	4400	∞	0

(2) Concentration 2·3*N*.

λ.	ε.	%*T*.	λ.	ε.	%*T*.
6800	∞	0	5400	0·20	63·1
6600	1·85	1·4	5200	0·17	67·6
6400	1·70	1·9	5000	0·10	79·4
6200	1·25	5·6	4800	0·17	67·6
6000	0·70	19·9	4600	0·32	47·8
5800	0·42	38·1	4400	0·83	14·7
5600	0·30	50·1			

(3) Concentration 0·93*N*.

λ.	ε.	%*T*.	λ.	ε.	%*T*.
7000	—	—	5400	0·10	79·4
6600	0·85	14·1	5200	0·08	83·1
6400	0·70	19·9	5000	0·05	89·1
6200	0·55	28·1	4800	0·08	83·1
6000	0·30	50·1	4600	0·10	79·4
5800	0·17	67·6	4400	0·22	60·2
5600	0·15	72·4			

Thus the limits of transmission for nickel sulphate are as given below.

Concentration.	Range of transmission.	Maximum % *T*.
5·28*N*	4400-6200 Å	53·7
2·3	4000-6800	79·4
0·93	All	89·1

Nickel Ammonium Sulphate.

λ.	ε.	% *T*.	λ.	ε.	% *T*.
7200	∞	0	5800	0·59	25·7
6400	1·60	2·5	5600	0·44	36·3
6200	1·26	5·4	5200	0·37	42·6
6000	0·88	13·1	4700	0·58	26·3

From the study of these nickel salts it will be clear that all of them show a maximum transmission in the region 5000Å. It is interesting to note that in case of nickel chloride the maximum transmission falls at 5200Å. This is evident, because the absorption in dilute solution in the case of the nickel salts is mainly due to common nickelous ions, but in case of nickel chloride, the anion also exerts its influence, especially in concentrated solutions, where the absorption is mainly due to nickel chloride molecule. We know that chlorine has absorption towards violet and hence the maxima for the transmission is shifted towards longer wave-length. When the solution becomes dilute even nickel chloride shows maximum transmission at 5000Å.

The ultraviolet transmission for nickel nitrate has been determined photographically and is recorded below.

Conc. (*M*) ...	4·16	2·08.	1·04	0·416	0·208	0·020
Range of transmission(Å)	3327-3427	3307-3598,	3248-3598	324-3860 and	2618-3860	2442 above

Thus nickel nitrate has absorption maxima in the region, 3860-4023Å in the ultra violet.

The author (Bhagwat, *U.P. Acad. Sciences*, 1932, 2, 67) has already discussed the use of nickel salts as light filters in combination with cobalt salts and have shown that these combinations transmit purely the ultraviolet region and hence are most suitable light filters for ultraviolet transmission. A short summary of these ultraviolet light filters is given below.

Ultraviolet and Visible Transmission.

Salt.	Time of exposure.	Visible.	Ultraviolet.
(1) 2·08*M*-$Ni(NO_3)_2$ + 1·83*M*-$CoCl_2$, each in 1 cm. quarter cell	4 hr.	5600-6300Å	3307-3598Å
(2) 4·16*M*-Ni $(NO_3)_2$ + 3·66*M*-$CoCl_2$	4	Nil	3420-3527 (faint)
(3) 2·08*M*-$Ni(NO_3)_2$ + 3·66*M*-$CoCl_2$	4	Nil	3307-3598
(4) 3·66*M*-$CoCl_2$	4	7100-7600Å	2618-4063

Nickel Nitrate.

(1) Concentration 4·16*M*.

λ.	e.	%*T*.	λ.	e.	%*T*.
4400	∞	0	5400	1·20	6·3
4450	faint ∞	0	5600	1·25	5·6
4500	3·20	0.068	5800	1·95	1·1
4600	2·45	0.35	5900	2·65	0·22
4800	1·30	5·0	6000	4·45	0·001
5000	1·10	7·9	6050	faint ∞	0
5200	1·17	6·7	6100	∞	0

(2) Concentration 2·08*M*.

λ.	e	%*T*.	λ.	e.	%*T*.
4300	∞	0	5600	0·60	25·1
4400	1·65	2·2	5800	0·96	10 9
4600	1·20	6·3	000	1·70	1·99
4800	0·57	26·9	6200	3·0	0·10
5000	0·52	30·2	6300	3·3	0·016
5200	0·55	28·1	6400	∞	0
5400	0·57	26·9			

(3) Concentration 1·04*M*.

λ.	e.	%*T*.	λ.	e.	%*T*.
4400	0·82	15·1	5600	0·28	52·4
4600	0·55	28·2	5800	0·47	33·8
4800	0·30	50·0	6000	0·83	14·7
5000	0·25	56·2	6400	1·90	1·23
5200	0·27	53·7	6600	2·20	0·63
5400	0·27	53·7	7000	2·45	0·35

(4) Concentration 0·208M.

λ.	e.	%T.	λ.	e.	%T.
4400	0·16	69·1	5800	0·09	81·5
4600	0·10	79·4	6000	0·16	69·2
4800	0·06	87·1	6200	0·29	51·3
5000	0·04	91·2	6400	0·36	43·6
5200	0·05	89·1	6600	0·40	39·8
5400	0·05	89·1	7000	0·45	35·5
5600	0·05	89·1			

My best and sincere thanks are due to prof. N. R. Dhar for his kind help and interest during the course of this work.

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On the p_H of Sols after Coagulation with Electrolytes.

By Satyaprasad Raychoudhury, Amiyakumar Sen and Asutosh Chatterjee.

The present paper records the following measurements:

(1) The pH of a ferric hydroxide sol (A) on the addition of increasing quantities of solid KCl, KBr, K_2SO_4 and KNO_3.

(2) The pH of an arsenious sulphide sol on the addition of increasing quantities of solid KCl and KBr.

(3) The pH and Cl' ion concentrations for (*a*) an aluminium hydroxide sol with the addition of increasing concentrations of K_2SO_4, $K_2C_2O_4$, KNO_3, $K_4Fe(CN)_6$, $NaNO_3$, $Na_2C_2O_4$, and KCl solutions, and (*b*) a ferric hydroxide sol in contact with K_2SO_4, $K_2C_2O_4$, KNO_3, $NaNO_3$ and $Na_2C_2O_4$ solutions.

Experimental.

Preparation of the Sols.

Ferric hydroxide sol.—10 C c. of a saturated solution of ferric chloride were added drop by drop to 600 c.c. of boiling conductivity water and the resulting sol was dialysed with frequent changes of distilled water until the dialysate was practically free from chloride. The sol was then stocked in wide mouthed Jena glass bottles.

Two such samples (A and B) were used in the course of the work in the present paper.

Arsenious sulphide sol.—A saturated solution of arsenious oxide was mixed with twice its volume of conductivity water. One litre of the diluted solution was added to a litre of conductivity water saturated with hydrogen sulphide, a gentle stream of which was continued till only a trace of arsenious acid was left free in the solution.

Aluminium hydroxide sol.—The aluminium hydroxide solution was prepared by adding slightly less than the equivalent amount of ammonium hydroxide solution ($N/10$) slowly and with vigorous stirring to a solution of aluminium chloride ($N/10$). The resulting sol was purified by dialysis in a parchment bag against repeated changes of distilled water, until a turbid sol was obtained.

Measurement of pH *values.*—The pH values were measured by the colorimetric method or by means of quinhydrone electrode or H_2

electrode against N-calomel electrode. A Hahn type (Hartmann and Braun, No. 16013) potentiometer was employed for measurement of *e.m.f.*

Measurement of Cl′ ion concentrations.—The Cl′ ion concentrations with both $Al(OH)_3$ and $Fe(OH)_3$ sols were measured by means of the Ag-AgCl electrode (*cf.* Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532).

Procedure.

In order to avoid the dilution of the sol on the addition of an electrolyte solution to a definite volume of the sol (ferric hydroxide sol A and the arsenious sulphide sol) weighed amounts of different solid electrolytes were added; the mixture was centrifuged and the p_H of the supernatant liquid determined either by the colorimetric or by the *e.m.f.* method.

In the case of ferric hydroxide sol (B) and aluminium hydroxide sol, 25 c.c. of the pure sol were in each case mixed with 25 c.c. of electrolyte and water and the mixtures were allowed to remain in contact for 16 hours. Where coagulation took place, the mixture was centrifuged and the p_H and Cl′ ion concentrations of the supernatant liquid were measured. Duplicate observations were taken in several cases. The results are reproducible. Concentration term in Tables I, II and III denotes concentration in g. equivalent per litre. 25 C c. of sol were taken in the case of the data in Tables I—III. All measurements were taken at room temperature.

TABLE I.

Ferric hydroxide sol (A).

KCl	Conc.	0·215	0·325	0·430	0·537
	p_H	4·88*	5·06*	5·35*	5·59*
KBr	Conc.	0·134	0·201	0·238	0·335
	p_H	5·20*	5·34*	5·42*	5·6*
K_2SO_4	Conc.	0·05	0·10	0·15	0·20
	p_H	6·8**	7·1**	7·3**	7·4**
KNO_3	Conc.	0·114	0·171	0·228	0·285
	p_H	6·0**	6·2**	6·3**	6·4**

* p_H taken by Hellige Immersion colorimeter.
** p_H taken by Hellige Disc comparator.

TABLE II.

Arsenious sulphide sol (original).

KCl	Conc.	0·215	0·322	0·537	0·752
	pH*	3·46	3·48	3·52	4.54
KBr	Conc.	0·134	0·201	0·335	0·469
	pH*	3·45	2·46	3·58	3·60

TABLE III.

Arsenious sulphide sol (doubly diluted, i.e., 1:1).

KCl	Conc.	0·285	0·322	0·537	6·752
	pH*	3·66	3·66	3·67	3·70
KBr	Conc.	0·134	0·261	0·305	0·460
	pH*	3·67	3·67	3·68	3·70

* H_2-electrode was employed. The liquid obtained after coagulation contained a trace of free arsenious oxide and no hydrogen sulphide could be detected with lead acetate. The H_2-electrode gave a consistent and steady e.m.f.

TABLE IV.

Change of p_H (by quinhydrone electrode) and Cl′ (by Ag-AgCl electrode) ions with different concentrations of electrolytes.

$Al(OH)_3$ sol. 0·1 *N* electrolytic concentration of mother electrolyte was used.

Composition.	K_2SO_4*		$K_2C_2O_4$**		KNO_3†		$K_4Fe(CN)_6$[1]		$NaNO_3$†		$Na_2C_2O_4$**		KCl
	pH.	Cl′ × 10^3.	pH.	Cl′ × 10^3.	pH.	Cl′ × 10^3.	pH.	Cl′ × 10^3.	pH.	Cl′ × 10^3.	pH.	Cl′ × 10^3.	pH.
25 c.c. sol + 25 c.c. H_2O	4·05	3·32	4·05	3·32	4·05	3·32	4·05	3·32	4·05	3·32	4·05	3·32	4·05
25 c.c. sol + 24 c.c. H_2O + 1 c.c. electrolyte	4·09	4·07	4·10	5·49	4·05	3·38	4·187	...	4·12	3·38	4·28	3·63	4·05
25 c.c. sol + 23 c.c. H_2O + 2 c.c. electrolyte	4·22	4·07	4·65	5·75	4·09	3·38	4·53	...	4·15	3·31	4·82	4·36	4·09
25 c.c. sol + 22 c.c. H_2O + 3 c.c. electrolyte	4·33	4·46	5·63	5·75	4·09	3·38	5·3	...	4·15	3·31	6·17	4·89	4·22
25 c.c. sol + 21 c.c. H_2O + 4 c.c. electrolyte	4·28	4·36	6·22	7·24	4·05	3·28	5·4	...	4·12	3·09	6·57	4·89	4·15

* Coagulation took place at all the given concentrations.
** No coagulation took place at all concentrations of the electrolytes excepting at the lowest one.
† No coagulation.

TABLE V.

Change of p_H (by Folien colorimeter) and Cl′ ion with Ag-AgCl electrodes with different concentrations of electrolytes.

Fe $(OH)_3$ Sol (B). 0·1N electrolytic concentration of mother electrolyte was used.

Composition.	K_2SO_4*		$K_2C_2O_4$*		KNO_3†		Na NO_3†		$Na_2C_2O_4$*	
	p_H.	Cl′ × 10^5.	p_H.	Cl′ × 10^5.	p_H.	Cl′ × 10^5.	p_H.	Cl′ × 10^5.	p_H.	Cl′ × 10^5.
25 c.c. sol + 25 c.c. H_2O	6·0	7·46	6·0	7·46	6·0	7·46	6·0	7·46	6·0	7·46
25 c.c. sol + 24 c.c. H_2O + 1 c.c. electrolyte	6·2	9·61	6·2-6·4	9 61	6·0	7·46	5·8-6·0	7·19	6·2	10·5
25 c.c. sol + 23 c.c. H_2O + 2 c.c. electrolyte	6·2	9·61	6·4-6·6	9·86	6·0	7·46	6·0-6·2	6·98	6·6-6·8	10·5
25 c.c. sol + 22 c.c. H_2O + 3 c.c. electrolyte	6·2	9·61	6·4-6·6	9·61	6·0	7·46	6·0-6·2	6·65	7·0-7·2	10·5
25 c.c. sol + 21 c.c. H_2O + 4 c.c. electrolyte	6·2	10·5	6·8-7·0	9·61	6·0	7·46	6·0	6·19	7·0-7·2	10·5

* Coagulation took place at all the given concentrations.
† No coagulation.

DISCUSSION.

Variation of p_H.

Ferric hydroxide sol (A) and arsenious sulphide sol (Tables I, III).—The p_H regularly increases with the amount of solid salt added. With arsenious sulphide the increase is much smaller. The concentration of the colloidal solution has also an influence on the p_H. Thomas and Whitehead (*J. Phys. Chem.*, 1931, **35**, 27) working with aluminium oxide sols observed a regular increase in the p_H below the coagulation concentration which apparently continues after the whole of the colloid is coagulated. Weiser (*J. Phys. Chem.*, 1931, **35**, 1) has observed that though the whole of the sulphate is taken up by the colloid (ferric oxide) so that none of it is left in the intermicellar liquid less than half the equivalent amount of chlorine is displaced from the colloidal particle. With increase in the concentration of the sulphate, the amount of chloride displaced increases linearly but suddenly rises near about the precipitation concentration wherafter it has the form of a typical adsorption isotherm. Weiser (*ibid.*, 1931, **35**, 1388) working with aluminium hydroxide sols has recently measured the p_H systematically at concentrations on both sides of the precipitation value. He obtained in most cases a rise in p_H but with potassium sulphate and a particular sol of aluminium oxide, he observed a lowering of the p_H. There is a difference between the experimental conditions used by the above authors and those used by us in that the solid salt has been used.

The order of the coagulation power of the anions for ferric oxide sols is as follows: sulphate > chloride > nitrate > bromide (*vide* Freundlich, *Z. physikal. Chem.*, 1903, **44**, 151). No such relationship exists between the p_H at equivalent concentrations of the anions and their coagulating powers. The same conclusion has been arrived at by Weiser (*loc. cit.*).

(*b*) *Ferric hydroxide sol (B) and aluminium hydroxide sol.*—Potassium and sodium nitrates have the least effect on the p_H value of both sols. These electrolytes cause no change of p_H with ferric hydroxide sol while with aluminium hydroxide sol there is a slight change in the p_H values; with the latter sol sodium nitrate increases the p_H slightly but perceptibly. A greater effect of $Na^{\cdot}$ as compared with $K^{\cdot}$ is also noticeable if we compare the two electrolytes $Na_2C_2O_4$ and $K_2C_2O_4$. Moreover, comparing KCl with KNO_3

the p_H is relatively greater for the chloride than for the nitrate. C_2O_4'' and SO_4'' have much greater effect on the p_H than Cl' or NO_3'. The difference may be partially explained if we assume the formation of $H_2C_2O_4$ and H_2SO_4. There is another possibility. The surface of the colloidal particles of ferric or aluminium oxide may contain simple or complex ion or aluminium ions of different valencies, *e. g.*, Fe^{+++}, $(FeOH)^{++}$ or $(FeOCl)^{++}$ or $(FeO)^{\pm}$. SO_4'' or C_2O_4'' ions being divalent the number of Fe^{++}or other higher valent ions disappear more quickly. Assuming an equilibrium between the ions on the surface with hydrogen ions in the solution it would be evident that the stability of higher valent ions which corresponds to higher stages of the dissociation of the base requires a p_H value lower than that for the lower valent ions. The disappearance of the higher valent ions would thus result in a diminution of the hydrogen ion concentration. The stability of these complexes would also depend on the chemical affinity *i. e.* the nature of the ions. Lastly the process of coagulation may affect the p_H by the entrainment of ions or by liberation of a part of the surface ions. SO_4'' has a greater coagulating action than C_2O_4'' on $Al(OH)_3$ sol, but a much smaller effect on the p_H and on the concentration of chlorine than C_2O_4''.

From Tables IV and V we find the following order of anions regarding their power to increase the p_H values:

For ferric hydroxide sol the order is $C_2O_4'' > SO_4'' > NO_3'$.

For aluminium hydroxide sol the order is $C_2O_4'' > SO_4'' > Cl' > NO_3'$

Variation of Cl′ ion Concentrations.

Ferric hydroxide sol (A) and aluminium hydroxide sol (vide Tables IV and V).—With $Al(OH)_3$ sol KNO_3 has practically no effect on Cl' ion concentrations. $NaNO_3$ shows a slight decrease and then a marked fall at higher concentrations of the electrolytes. With K_2SO_4 and $Na_2C_2O_4$ there is a considerable increase in Cl' ion concentrations. C_2O_4'' has somewhat greater effect as compared to SO_4''. It appears that with SO_4'', Cl' is liberated as if on by stages while with C_2O_4'', Cl' is liberated continually. This difference may be apparent and not real. It is remarkable that in both cases the effect of electrolytes on the variation of p_H and Cl' is somewhat parallel. This may mean breakdown of the original complexes with consequent liberation of Cl' ions and an increase in the p_H on the formation of stabler complexes of lower valency. With aluminium hydroxide sol

$K_2C_2O_4$ has a greater effect, in increasing the Cl′ ion concentrations than $Na_2C_2O_4$; with ferric hydroxide sol the opposite behaviour is observed.

Curiously enough, KNO_3 does not increase the Cl′ ion concentrations. $NaNO_3$ increases the Cl′ ion concentrations of Al $(OH)_3$ sol when the concentration of electrolyte is very low but a fall of the Cl′ ion increase is noticed at higher concentrations. In the case of Fe $(OH)_3$ sol there is a continuous fall in Cl′ ion concentrations at all concentrations of added electrolyte. The difference in the effects of KNO_3 and $NaNO_3$ on the pH and in the liberation of the chlorine has some points of similarity. C_2O_4'' and SO_4'' increase the Cl′ ion concentrations of $Fe(OH)_3$ sol.

The order in which the above anions increases the chlorine ion concentration is as follows:

$$Fe(OH)_3 \text{ sol} \qquad SO_4'' \gtrsim C_2O_4'' > NO'_3$$

$$Al(OH)_3 \text{ sol} \qquad C_2O_4'' \gtrsim SO_4'' > NO'_3$$

It will be seen that there is no exact parallelism between coagution capacity, the liberation of chlorine ions and pH. The reaction that takes place is thus complicated and theoretically one can conceive the following reactions being responsible for the ultimate result: (*a*) the reaction of the primarily or electrically adsorbed ion and those in the mobile layer with those in solution ; (*b*) the transformation of SO_4'' or C_2O_4'' ions to HSO_4' or HC_2O_4' in the intermicellary liquid itself, and (*c*) the entrainment or liberation of ions and consequent hydrolytic and other changes resulting from agglomeration itself.

SUMMARY.

1. The pH of the supernatant liquid after coagulation of ferric hydroxide (A) and arsenious sulphide sols depends on the nature of the coagulating electrolyte and to a less extent on its amount. With both sols the pH increases on addition of larger amounts of *solid* electrolytes. With arsenious sulphide sol, the increase in pH is very slight.

2. With ferric hydroxide sol (B) and aluminium hydroxide sol, there is a tendency for increase in pH and Cl′ ion concentrations on addition of increasing concentrations of electrolytes.

(*a*) Potassium and sodium nitrates have the least effect on the p_H value of both sols.

(*b*) The following orders of anions for increasing the p_H have been observed :

Ferric hydroxide sol $C_2O_4'' \geq SO_4'' \geq NO'_3$

Aluminium hydroxide sol $C_2O_4'' \geq SO_4'' \geq NO'_3$

(*c*) The order in which the anions increase the Cl' ion concentrations are as follows:

Ferric hydroxide sol $SO_4'' \geq C_2O_4'' \geq NO'_3$

Aluminium hydroxide sol $C_2O_4'' \geq SO_4'' \geq NO'_3$

(*d*) Potassium nitrate has got no effect in increasing the Cl' ion concentration of sols.

(*e*) There is no exact parallelism between coagulating capacity, the liberation of Cl' ions and the p_H.

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Influence of Attached Rings on the Formation and Stability of Heterocyclic Compounds. Part II.

By Tejendra Nath Ghosh.

In part I (*J. Indian Chem. Soc.*, 1933, 10, 583) a hypothesis has been developed on the basis of some experimental facts that the fused benzene ring helps ring-formation and the effect appears to increase with the increase in the number of benzene rings. In order to confirm further this idea, the present investigation has been undertaken.

β-Arylthiocarbamidopropionic acid (I) is obtained from β-amidopropionic acid and *iso*thiocyanate. It does not, however, suffer any change even when boiled with strong hydrochloric acid for a long time.

$$\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-CO_2H \end{array} \xrightarrow{\text{RNCS}} \begin{array}{l} CH_2-NH-CS-NHR \\ | \\ CH_2-CO_2H \end{array}$$

(I)

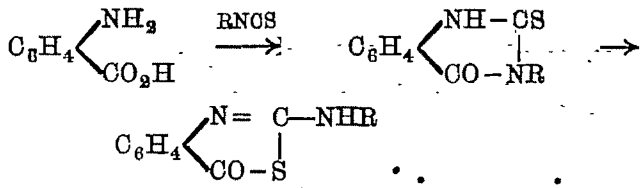
β-Phenyl-β-arylthiocarbamidopropionic acid (II), obtained from β-amido-β-phenylpropionic acid and *iso*thiocyanate, yields, on treatment with acetic anhydride, a thiazine derivative (III) which cannot be desulphurised by oxide of mercury. The thiazine derivative (III) is easily hydrolysed to compound (II) by normal alkali even in the cold.

$$\begin{array}{l} PhCH-NH-CS-NHR \\ | \\ CH_2-CO_2H \end{array} \underset{\text{alkali}}{\overset{Ac_2O}{\rightleftharpoons}} \begin{array}{l} PhCH—N=C-NHR \\ |\qquad\qquad\;\; | \\ CH_2-CO-S \end{array}$$

(II) (III)

It has already been found (Ghosh, *J. Indian Chem. Soc.*, 1930, 7, 981) that anthranilic acid gives a quinazoline derivative with *iso*thiocyanate, instead of *o*-arylthiocarbamidobenzoic acid and that this quinazoline is converted into a benzothiazine derivative by the action

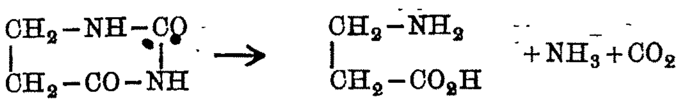
of strong sulphuric acid. The above benzothiazine derivative cannot be hydrolysed even by 10 % alcoholic potash or strong acids.



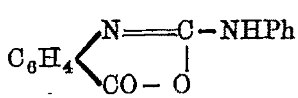
The dipotassium salt of *o*-benzoyleneurea, obtained by the action of hot alcoholic potash, gives the corresponding diethyl derivative (IV) (Bogert and May, *J. Amer. Chem. Soc.*, 1909, **31**, 512) showing that alkali cannot bring about the hydrolysis of *o*-benzoyleneurea.

(IV)

β-Lactylurea, on the other hand, is decomposed, on being similarly treated with alkali, into the potassium salt of *β*-aminopropionic acid.

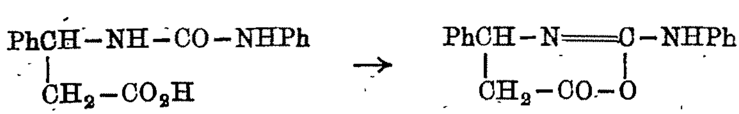


o-Phenylcarbamidobenzoic acid (Paal, *Ber.*, 1894, **27**, 978) yields, on treatment with acetic anhydride, a benzoxazine derivative (V).



(V)

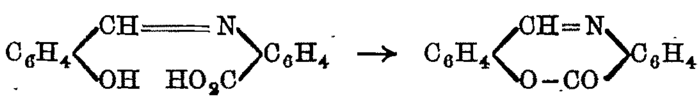
Similarly *β*-phenyl-*β*-phenylcarbamidopropionic acid (VI), obtained from *β*-amido-*β*-phenylpropionic acid and phenyl *iso*cyanate, yields with acetic anhydride an oxazine derivative (VII).



(VI) (VII)

Both of the above compounds (V and VII) are slowly hydrolysed to the corresponding acids in decinormal alkali at ordinary temperature but at higher temperature the conversion is too rapid to allow any comparative study of the velocity coefficient.

Salicylidene-anthranilic acid (VIII) yields with acetic anhydride a lactone (IX) which remains unchanged in presence of cold normal alkali. This remarkable stability of the eight membered lactone ring (IX) is evidently due to the presence of the two fused benzene rings.

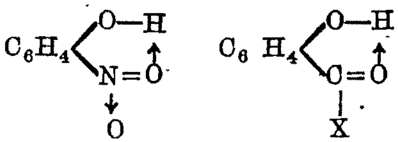


(VIII) (IX)

Now the very fact that straight chain compounds (I and II) are always obtained from β-amidopropionic acid or its substitution products with thiocarbimides, whereas under exactly similar conditions, quinazolines are obtained from anthranilic acid and thiocarbimides and that benzothiazine and *o*-benzoyleneurea are much more stable than the thiazine derivative (III) and β-lactylurea respectively, shows conclusively how the fused benzene ring helps ring-formation and stabilises the heterocyclic systems.

From the recent velocity coefficient measurements of Guha-Sircar (*J. Chem. Soc.*, 1927, 600, 1258) it is found that the coefficient for the hydrolysis of homophthalimide is nearly half of that of glutarimide, which, in the light of the observations now made, can be explained as being due to the presence of the fused benzene ring in homophthalimide. Further, there are many heterocyclic compounds known the formation of which can be explained on the basis of the hypothesis developed in this paper. It is well known that in *ortho*-substituted phenols *e.g.*, *o*-hydroxybenzoic acids, their esters and aldehydes, *o*-nitrophenols, the polar character due to the hydroxylic hydrogen is absent in much the same way as if this hydrogen were replaced by methyl. Philip (*J. Chem. Soc.*, 1903, 83, 820) has found that *o*-nitrophenol does not condense with aniline as the *m*- and *p*-isomerides do. On the basis of electronic theory of valency, Sidgwick and Callow (*J. Chem. Soc.*, 1924, 125, 532) have explained the peculiar behaviour of the *ortho*-substituted phenols of the above type on the assumption that the hydroxylic hydrogen participates in a chelate ring-formation which can only happen if the

hydrogen forms a co-ordinate link with some atom of the second substituent thus:

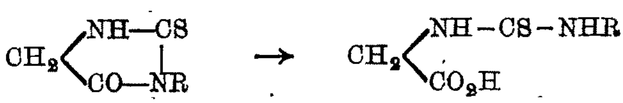


($X=OH$, H, O alk)

These six membered rings belong to the most stable type of chelate ring known. It is further known that the hydroxyl group which behaves in a peculiar manner when attached to the benzene ring, retains its normal and characteristic property when attached to a straight chain system, showing firstly, that there is no formation of chelate ring in the latter and secondly, that the formation of the chelate ring is evidently due to the presence of the fused benzene ring.

In order to explain this behaviour of the fused benzene ring in helping ring-formation and promoting ring-stability of heterocyclic systems, reference may be made to a very interesting paper of Mills and Nixon (*J. Chem. Soc.*, 1930, 2510) who have shown by mathematical calculations of the angles of the carbon atoms that round the benzene ring adjacent valancies will be closer when the carbon atoms are joined by a single bond. In the open-chain series there being no such influence, the ring-formation does not take place so readily.

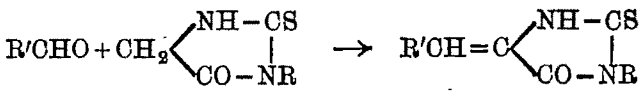
Some further interesting examples of the stability of analogous heterocyclic systems have been observed in cases where a double bond exists just outside the heterocyclic ring. When glycine reacts with *iso*thiocyanates (*cf.* Aschan, *Ber.*, 1884, **17**, 420) in each case a mixture of the corresponding diazole derivative (X) which is soluble in alkali and a small quantity of diarylthiourea has been obtained. The diazole is easily hydrolysed by equimolecular quantity of alcoholic alkalis yielding arylthiocarbamidoacetic acid



(X) (XI)

(XI). The diazole contains a reactive methylene group and readily reacts with aldehydes to give the compound (XII) which,

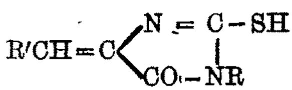
however, is remarkably resistant even towards 10% alcoholic alkalis.



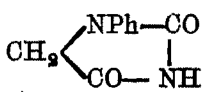
(XII)

This stability is evidently due to the double bond which has been introduced in compound (XII).

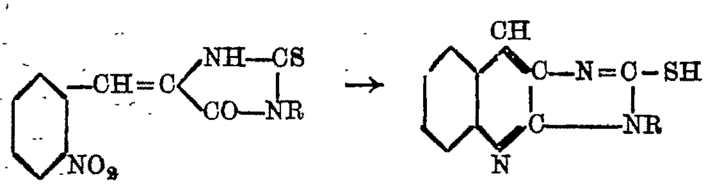
It is interesting to note that the compound (XII) is not desulphurised by oxide of mercury, whereas the original diazole (X) is easily desulphurised, showing firstly that the compound (XII) exists only in the tautomeric form and secondly, that the reactivity of the



methylene group is conditioned by the presence of the grouping $-CO-CH_2-N=\overset{|}{C}-$ and has been increased by duplication within a ring (*cf.* Higginbotham and Lapworth, *J. Chem. Soc.*, 1922, **121**, 2826). This observation is confirmed by the fact that neither arylthiocarbamidoacetic acid nor phenylhydantoin reacts with aldehydes under usual conditions.



The compound (XIII), obtained from the diazole (X) and *o*-nitrobenzaldehyde, yields a quinoline derivative (XIV) on reduction with tin and hydrochloric acid (*cf.* Baeyer and Drewson, *Ber.*, 1883, **16**, 2207).



(XIII) (XIV)

The stability of compounds of the type (XII) compares favourably with that of the fused benzene-heterocyclic systems described in the

preliminary portion. Although it is not possible at this stage to offer any explanation for this similarity of behaviour in the two types of compounds, it may be just likely that the stability of the compounds of the type (XII) is conditioned by similar steric considerations as offered by Mills and Nixon (*loc. cit.*).

Experimental.

β-o-Tolylthiocarbamidopropionic acid (I, R=*o*-tolyl).—β-Aminopropionic acid (2·2 g.), prepared according to the method of Hoogewerff and Dorp (*Rec. Trav. Chim.*, 1891, **10**, 4) was dissolved in water to which an alcoholic solution of *o*-tolyl *iso*thiocyanate (8·7 g.) was added and the solution was boiled under reflux for about an hour and cooled when a solid came out which crystallised from dilute alcohol in colourless prisms, m.p. 144-45° (decomp.). (Found: N, 11·49. $C_{11}H_{14}O_2N_2S$ requires N, 11·76 per cent). It is soluble in sodium bicarbonate solution and does not suffer any change even when boiled with strong hydrochloric acid for a long time. It is desulphurised to an alkali insoluble compound (m.p. 236-37°) which could not be further studied due to poor yield.

β-p-Tolylthiocarbamidopropionic acid (I, R=*p*-tolyl) was crystallised from dilute alcohol in colourless prisms, m. p. 151-52° (decomp.). (Found: N, 11·52. $C_{11}H_{14}O_2N_2S$ requires N, 11·76 per cent).

β-Phenyl-β-phenylthiocarbamidopropionic acid (II, R=phenyl).—An alcoholic solution of β-phenylpropionic acid (8·8 g.), prepared according to the method of Posner (*Ber.*, 1905, **38**, 2320) and phenyl *iso*thiocyanate (2·7 g.) was heated under reflux for about 2 hours and evaporated when a crystalline mass was obtained which dissolves readily in sodium bicarbonate solution and is precipitated by acids. It is very soluble in alcohol, ether and acetic acid and was crystallised from very dilute acetic acid in colourless prisms, m. p. 145-43° (decomp.). (Found: S, 10·41. $C_{16}H_{16}O_2N_2S$ requires S, 10·66 per cent). It is easily desulphurised by yellow oxide of mercury and does not suffer any change even when boiled with strong hydrochloric acid.

1-Phenylamino-3-keto-5-phenyl-2:6-thiasine (III, R=phenyl).—2 G. of the above compound (II, R=phenyl) were heated with acetic anhydride (80 c.c.) for about an hour when the clear solution,

on cooling, deposited a colourless crystalline mass. A further quantity of the substance was obtained by adding water to the acetic anhydride solution which was being stirred vigorously. It was crystallised from acetic acid in colourless needles, m. p. 232-33° (decomp.), yield 1·2 g. (Found: S, 11·07. $C_{16}H_{14}ON_2S$ requires S, 11·34 per cent). It is not desulphurised by oxide of mercury. When it is kept in contact with normal caustic potash solution for 2-3 hours a clear solution is obtained which, on acidification, yields a colourless precipitate crystallising from dilute acetic acid in prisms, m. p. 145-46° (decomp.). The identity of this compound with the compound (II, R=phenyl) was confirmed by mixed m. p., properties and finally by analysis.

β-Phenyl-β-o-tolythiocarbamidopropionic acid (II, R=*o*-tolyl) was crystallised from dilute acetic acid in colourless prisms, m. p. 154-55° (decomp.). (Found: S, 9·88. $C_{17}H_{18}O_2N_2S$ requires S, 10·19 per cent).

1-o-*Tolylamino-3-keto-5-phenyl-2:6-thiazine* (III, R=*o*-tolyl) was crystallised from acetic acid in colourless needles, m. p. 169°. (Found: S, 10·53. $C_{17}H_{16}ON_2S$ requires S, 10·81 per cent). It is also easily hydrolysed by caustic potash solution.

Diethyl derivative of o-benzoyleneurea (IV).—*o*-Benzoyleneurea (1 mol.) was dissolved in alcoholic potash (caustic potash, 2 mols.) which was heated under reflux for about an hour and then evaporated almost to dryness. The potassium salt thus obtained is very soluble in cold water from which it is precipitated by the addition of large quantity of alcohol in beautiful colourless plates, m. p. above 300°. On acidification it yielded *o*-benzoyleneurea. It was dissolved in the smallest quantity of water to which an alcoholic solution of ethyl iodide (2 mols.) was added and the solution was boiled under reflux for about half an hour and then evaporated. The product was crystallised from dilute alcohol in beautiful colourless slender needles, m. p. 108°. (Found: N, 12·82. $C_{12}H_{14}O_2N_2$ requires N, 12·84 per cent). Bogert and May (*loc. cit.*) give 105-6° as the m. p. of the compound.

Action of alkali on β-lactylurea.—*β*-Lactylurea (1 mol.) was dissolved in alcoholic potash (caustic potash being 2 mols), heated under reflux for about an hour and evaporated almost to dryness. The potassium salt was dissolved in cold water and acidified when an effervescence of carbon dioxide began. No solid, however, came out. From the clear solution *β*-aminopropionic acid was isolated accord-

ing to the method of Hoogewerff and Dorp (*loc. cit.*) and identified with a genuine sample.

1-Phenylamino-3-keto-4:5-benzo-2:6-oxazine (V).—An acetic anhydride solution of *o*-phenylcarbamidobenzoic acid (5 g.) was heated under reflux for about half an hour. The clear solution, on cooling, gave a mixture of a quinazoline derivative (already prepared by Paal, *loc. cit.*) and the oxazine derivative, from which the latter was separated by treatment with very dilute alkali and crystallised from alcohol in colourless prisms, m. p. 124-25°, yield 1·5 g. (Found: N, 11·48. $C_{14}H_{10}O_2N_2$ requires N, 11·76 per cent).

β-Phenyl-β-phenylcarbamidopropionic acid (VI).—β-Amido-β-phenylpropionic acid (3·3 g.) was dissolved in dilute alcohol to which phenyl *iso*cyanate (2·3 g.) was added. The precipitate was crystallised from alcohol in colourless needles, m.p. 168-69° (decomp.), yield 4·5 g. (Found: N, 9·72. $C_{16}H_{16}O_3N_2$ requires N, 9·85 per cent).

1-Phenylamino-3-keto-5-phenyl-2:6-oxazine (VII).—The method of preparation was the same as in the case of the compound (III). The product was crystallised from alcohol in colourless slender needles, m. p. 221-22°. (Found: N, 10·31. $C_{16}H_{14}O_2N_2$ requires N, 10·52 per cent).

Salicylidene-anthranilic acid (VIII).—An acetic acid solution of anthranilic acid (2·7 g.) and salicylaldehyde (2·4 g.) was heated under reflux for half an hour when a yellow crystalline mass was obtained which further crystallised from acetic acid in yellow needles, m. p. 188-90°, yield 3·5 g. (Found: N, 5·53. $C_{14}H_{11}O_3N$ requires N, 5·81 per cent). It is soluble in aqueous solution of sodium bicarbonate.

Action of acetic anhydride on the above compound (VIII): *Formation of compound* (IX).—The method of procedure was the same as in the case of the compound (III). The product was crystallised from alcohol in colourless prisms, m. p. 156-57°. (Found: N, 6·08. $C_{14}H_9O_2N$ requires N, 6·27 per cent). It is not readily soluble in cold normal alkali but when kept in presence of the cold alkali for a day it goes into solution which, on acidification, yields the original compound (VIII). When it is heated with strong hydrochloric acid, the solution, on cooling, deposits a colourless crystalline mass which has been identified to be anthranilic acid hydrochloride.

*1-Keto-4-thioketo-5-*p*-tolyl-3:5-diazole* (X, R=*p*-tolyl).—Glycine (3·8 g.) was dissolved in the smallest quantity of hot water to which

an alcoholic solution of *p*-tolyl*iso*thiocyanate (7·5 g.) was added. The solution was boiled under reflux for about an hour and then evaporated to dryness. The crystalline precipitate was treated with cold dilute caustic potash solution when a small portion remained undissolved. The rose-coloured alkaline solution, on acidification, gave a yellowish precipitate which crystallised from alcohol in yellowish needles, which darken at 205° emitting strong smell of mercaptan and melt completely at 229-30°, yield 8 g. (Found: N, 13·41. $C_{10}H_{10}ON_2S$ requires N, 13·59 per cent).

The product insoluble in alkali was crystallised from alcohol in colourless plates, m.p. 176°. The identity of this compound with di-*p*-tolylthiourea was proved by taking a mixed melting point and finally by analysis.

1-*Keto-4-thioketo-5-*o*-tolyl-3:5-diazole* (X, R=*o*-tolyl) was crystallised from alcohol in yellowish needles, m.p. 145-46°. (Found: N, 13·37. $C_{10}H_{10}ON_2S$ requires N, 13·59 per cent). The alkali-insoluble compound was similarly proved to be di-*o*-tolylthiourea.

p-*Tolylthiocarbamidoacetic acid* (XI, R=*p*-tolyl).—The above compound (X, R=*p*-tolyl ; 3·8 g.) was dissolved in 100 c.c. of alcohol containing 1·3 g. of caustic potash. The rose-coloured clear solution was heated under reflux for about an hour and evaporated to dryness. The solid was washed several times with absolute alcohol and crystallised from water in colourless prisms. It is the potassium salt of *p*-tolylthiocarbamidoacetic acid, colours pink on heating and melts at 240° (decomp.). (Found: N, 10·46. $C_{10}H_{11}O_2N_2SK$ requires N, 10·69 per cent). The *free acid* was obtained as a colourless precipitate when a cold aqueous solution of the above potassium salt was acidified with dilute hydrochloric acid. It crystallised from hot water in colourless rectangular plates, m.p. 147-48° (decomp.). (Found: N, 12·31. $C_{10}H_{12}O_2N_2S$ requires N, 12·50 per cent). It is readily soluble in sodium bicarbonate solution.

o-*Tolylthiocarbamidoacetic acid* (XI, R=*o*-tolyl) was crystallised from dilute alcohol in colourless prisms, m.p. 141-42° (decomp.). (Found: N, 12·28. $C_{10}H_{12}O_2N_2S$ requires N, 12·50 per cent).

1-*Keto-2-benzal-4-thioketo-5-phenyl-3 : 5-diazole* (XII, R=R′=phenyl).—A glacial acetic acid solution of benzaldehyde (2·1 g.) and the diazole derivative (X, R=phenyl ; 3·8 g.) was heated under reflux for about an hour. The clear solution, on cooling, deposited a crystalline mass which further crystallised from alcohol in beautiful

yellowish plates, m.p. 196-97°. It is soluble in dilute alkali and is precipitated by acids. (Found: N, 10·13. $C_{16}H_{12}ON_2S$ requires N, 10·0 per cent). It is not desulphurised by oxide of mercury and remains unchanged even when heated with 10 % alcoholic potash.

1-*Keto-2-benzal-4-thioketo-5-*p*-tolyl-3:5-diazole* was crystallised from alcohol in yellowish plates, m.p. 180-81°. (Found: N, 9·31. $C_{17}H_{14}ON_2S$ requires N, 9·52 per cent).

1-*Keto-2-*o*-nitrobenzal-4-thioketo-5-phenyl-3:5-diazole* (XIII, R= phenyl).—The product, obtained by condensing *o*-nitrobenzaldehyde with the diazole derivative (X, R= phenyl) in acetic anhydride solution, was crystallised from alcohol in yellow needles, m.p. 216-18°. (Found: N, 12·64. $C_{16}H_{11}O_3N_3S$ requires N, 12·92 per cent).

Reduction of the above compound (XIII): *Formation of compound* (XIV, R=phenyl).—The above compound (6 g.) was heated under reflux with strong hydrochloric acid (70 c c.) and granulated tin (25 g.) for about 3 hours when a clear solution was obtained. The solution was then diluted with water when a precipitate came down which crystallised from dilute alcohol in brownish white needles, m.p. 186°, yield 1·5 g. (Found: N, 14·88. $C_{16}H_{11}N_3S$ requires N, 15·16 per cent). It is soluble in alkali and is precipitated by acids.

Further work in this line is in progress.

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Chemical Reactivity and Light Absorption Part I.

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It can now be stated with a certain amount of definiteness that the appearance of a continuous absorption (non-quantised absorption) spectrum of a gas is always a case of photochemical dissociation taking place in the gas. Moreover, convergence limits and continuous absorption have up till now only been observed for those molecules in which the binding forces are appreciably weakened by absorption.

According to Kuhn and Franck, one normal and one excited metastable atom are produced from the dissociation of the halogen molecules. Naturally, more energy is required for this type of dissociation than in the cases where the products of dissociation are two normal atoms. Mecke (*Trans. Faraday Soc.*, 1931, 27, 359) has drawn the following conclusion from his observations on molecular spectra and photochemical dissociation:

" On the short wave side of the band convergence limit and in a spectral region distinguished by continuous absorption and by the fact that the molecules cease to fluoresce, a photochemical reaction with theoretical quantum yield can take place (chain reactions are of course excluded from this last statement). At the entrance to this region is a spectral region, more or less wide, in which the absorbed energy is not sufficient to produce primary dissociation but which nevertheless is large enough when transferred by impact, to produce dissociation by sensitising. In this spectral region as is usual for reactions with excited molecules we obtain only a fraction of the theoretical yield for quantum; as the convergence limit is approached, however, this yield rapidly attains the maximum value".

The phenomenon of sensitised decomposition of simple molecules is more or less allied to the phenomenon of predissociation studied by Victor Henri with polyatomic molecules,

It appears, therefore that increase in the light absorption by a molecule is associated with its increased reactivity and loosening of the binding forces. Conversely when a molecule becomes more reactive, it is likely to absorb light more markedly. Henri (Compare Debye, "Structure of Molecules," Blackie & Son, 1932) has shown that the absorption spectra of a number of molecules pass from a fine structure to a blurred one consisting of diffuse bands in the short wave-length side of the spectrum. The condition of the molecule in which the bands are diffused has been called the *predissociation*, as it has been observed that in this condition the molecules are chemically reactive and can decompose. The limit of predissociation is assumed to set the upper limit of dissociation of a molecule.

Henri has reported that an increase of temperature displaces the limits of dissociation towards the visible region and the radiations of the region of predissociation causes photochemical reaction or chemical sensitisation of the molecules.

From the researches of Henri and others it is clear that on increasing the temperature, the amount of light absorption increases and the molecules dissociate on illumination by radiations of longer wave-lengths. Thus with acetaldehyde, the absorption spectrum at the laboratory temperature consists of large number of sharp bands with rotational structure between 3484 to 3050Å. Near 3050Å the bands become blurred rapidly due to predissociation of the molecules and about 60 diffuse bands reaching upto 2823Å have been measured. Also there is superimposed on these diffuse bands, a broad continuous band starting at about 3080Å with a maximum at 2850Å and subsequently falling off more and more on the ultraviolet side. If acetaldehyde vapour is heated to 200°, feeble diffuse bands appear between 3500 and 3200Å with a strong continuous absorption reaching far into the ultraviolet.

When acetaldehyde vapour is illuminated at the laboratory temperature, decomposition takes place into CO and CH_4 only when the wave-length is 3002Å or shorter; whilst at 200°, acetaldehyde vapour can be photolysed by radiations of wave-length exceeding 3100Å. According to Hinshelwood and Hutchinson (*Proc. Roy. Soc.*, 1926, **A**, **111**, 380), acetaldehyde vapour can be thermally decomposed at 430°. Similar behaviour has been observed with other aldehydes, CS_2, NH_3, NO_2, sulphur and other substances.

It appears, therefore, from these researches on photochemical decomposition and predissociation that the increase in the chemical reactivity of a substance by increase of temperature is associated with an increased light absorption, specially of ultraviolet light. Moreover, increased temperature of the molecules sensitises them towards their decomposition by longer wave-lengths. Hence the weakening of the bindining forces of molecules and thus making them unstable is associated with increased light absorption by the molecules. These researches on predissociation and chemical decomposition have been solely confined to pure individual substances and not to mixtures with which chemists are mainly concerned. Let us examine the problem from the point of view of mixtures of two or more substances.

It is well known that in their experiments on the photochemical combination of hydrogen and chlorine, Bunsen and Roscoe reported that the absorption of light by chlorine was increased by the presence of hydrogen, although Burgess and Chapman (*J. Chem. Soc.*, 1906, **89**, 1402) could not detect any difference in the absorption of pure chlorine or its mixture with air or hydrogen.

On the other hand, Weigert (*Z. physikal. Chem.*, 1926, **120**, 215) has shown that radiations of mean wave-length 5900Å, and Dhar and Bhagwat (*Z. anorg. Chem.*, 1930, **190**, 415) have reported that radiations of wave-lengths 5750-5800Å, 6650Å, and 7304Å can accelerate the reaction between chlorine and hydrogen, although the calculated maximum wave-length capable of initiating the reaction has the value 5400Å. This value has been obtained from the heat of dissociation of a gram molecule of chlorine having the value 52500 calories. According to Mecke (*loc. cit.*) the limits of sensitised decomposition and photochemical dissociation for chlorine molecules are 5000Å and 4780Å respectively.

Several years ago, Sirk (*Z. physikal. Chem.*, 1908, **61**, 545) observed that chlorine and hydrogen combine in the dark when heated to 258°. The temperature coefficient of this thermal reaction has the value 1·6 for a 10 degree rise between 258° to 268°. On applying the Perrin-Lewis radiation hypothesis, the value 10,714Å is obtained for the activation of the reaction. Moreover, Sachtleben (Diss. Hannover, 1914) obtained the temperature coefficient 2·04 for a 10° rise between 146°·5 and 160°·1 for the thermal reaction

between chlorine and hydrogen and hence the limiting wave-length obtained from this result is 11,110Å, a value almost identical to that of Sirk (compare Christiansen, *Z. physikal. Chem.* 1929 **B**, **2**, 405). It appears, therefore, that the theoretical limiting wave-length for including the photochemical combination of chlorine and hydrogen is of the order of 10,000Å and the experimental value is near 7000Å. It is well known that a greater amount of energy is necessary for the photo-reaction than the thermal one with many decomposition reactions and a part of the light energy absorbed may be lost as fluorescence. It is of interest to note that Norrish (*J. Chem. Soc.*, 1927, 761; 1929, 1604, 1611) has concluded that far more energy is required to decompose nitrogen peroxide photochemically than thermally and has been able to observe fluorescence with nitrogen peroxide. Similarly fluorescence has been observed in acetaldehyde and acetone and formaldehyde vapour (*cf.* Leighton and Blacet, *J. Amer. Chem. Soc.*, 1933, **55**, 1766; Damon and Daniels, *ibid.*, 2363; Crone and Norrish, *Nature* 1933, **132**, 241; Herzberg and Franz, *Z. physik*, 1932, **76**, 720). It is clear, therefore, from the foregoing remarks that the presence of hydrogen sensitises the decomposition of chlorine molecules and makes them reactive in radiations of longer wave-lengths. The careful measurements of the absorption spectra of chlorine by von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71)* show that the light absorption from yellow to red, reaches a maximum between 6140 to 6430Å. It appears to the authors that accurate experiments on the absorption spectrum of a mixture of hydrogen and chlorine are likely to reveal that the absorption of light by chlorine is increased by the addition of hydrogen.

From our experiments on the kinetics of the iodine oxalate reaction, we have observed that the reaction is markedly accelerated by infra-red radiations of wave-lengths 8500Å and 8750Å and the maximum wave-length calculated from the temperature coefficient of the dark reaction was the value 8600Å. The limits of sensitised decomposition and photochemical decomposition with iodine molecules are 8050Å and 4995Å respectively. It appears, therefore, that the presence of oxalate markedly sensitises the decomposition of iodine molecules, which become reactive in radiation of longer wavelengths on the addition of oxalate using copper arc. We have carefully photographed the absorption spectra of $N/1700$ aqueous iodine

and $N/2$-potassium oxalate solutions separately and a mixture containing 10 c.c. N-$K_2C_2O_4$ and 10 c.c. $N/850$ aqueous iodine and we find that the iodine solution alone shows almost complete absorption from 2700Å, whilst with the oxalate solution complete absorption begins from 3000Å. In the case of the mixture of the iodine and oxalate, almost complete absorption starts nearly from 3826Å. These results, showing that the absorption of light by a solution of an oxalate is appreciably increased by the addition of dilute iodine solution, are of great interest from the view point of the nature of chemical reactivity.

In other words, the sensitisation of an oxalate solution by iodine is associated with marked increase of light absorption in the ultraviolet.

Many years ago Henri and Landau (*Compt. rend.*, 1913, **158**, 181) showed that the absorption of ultraviolet light in the region 3200-2700Å by a solution of oxalic acid is markedly increased by the addition of uranyl salts. Recently Ghosh and collaborators (*J. Indian Chem. Soc.*, 1927, **4**, 353; 1928, **5**, 191, 569) have carried on important quantitative measurements of the extinction coefficients of uranyl salts, ferric salts, and mercuric salts with varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, citric, and mandelic acids in the region 2300-3500Å and have observed that the extinction coefficients of the mixtures of organic acids and the above salt solutions are always considerably greater than the sum of those of the organic acids and the salt solutions considered separately. Moreover, it is well known that almost all organic acids are oxidised by uranyl, ferric and mercuric salts even in presence of visible light.

Allmand and Reeve (*J. Chem. Soc.*, 1926, 2834) obtained the following quantum yields in the decompositions of oxalic and formic acid solutions used as sensitiser:

	Oxalic acid.			Formic acid.		
Wave-length in Å ...	2650	3000	3650	2600	3000	3600
Quantum yield ...	0·0100	0·0041	0·00095	2·7	1·06	very small

The quantum yield of the decomposition of these acids is generally greater in the presence of the sensitisers.

It is not yet certain what the predissociation limits of acetic acid or the other organic acids are, but Henri has given the following values for some aldehydes.

Molecule.	Predissociation observed.	Cal.
H·CHO	2670 Å	107
CH_3CHO	3050	95
C_6H_5CHO	2550	110

Ghosh and collaborators (*loc. cit.*) have obtained the following results on light absorption with different organic acids.

M/20-Acid →	Formic	Acetic	Propionic	Oxalic	Malonic	Succinic
Beginning of absorption →	2445 Å	2445 Å	2445Å	3274 Å	2507Å	2445Å
M/20-Acid →	Glycollic	Lactic	Tartaric	Mandelic		Citric
Beginning of absorption →	2722Å	2507Å	2600Å	2800Å	shorter than 2722Å	

It appears that these wave-lengths are predissociation limits of these organic acids in the gaseous states and they are decomposed in these radiations. It seems justifiable to apply the results obtained in the gaseous state to solutions because in many cases it has been observed that the absorption spectra of molecules in the gaseous state and in the dissolved condition are identical. Thus Urey, Dawsey and Rice (*J. Amer. Chem. Soc.*, 1929, **51**, 1371) have measured the absorption coefficients of a solution of hydrogen peroxide for wave-lengths from 3750-2150Å and those of its vapour for wave-lengths 2150-2750Å. The two absorption curves between 2150-2750Å appear to be identical. Moreover, Allmand, Cunliffe and Maddison (*J. Chem. Soc.*, 1927, 655) have reported that the values of the extinction coefficient of chlorine in aqueous solution are very close to those of gaseous chlorine. Also in recent years it is being realised more and more that the kinetics of the chemical reactions taking place in solution are fundamentally the same as those of the same substances in the gaseous condition. Thus the decomposition of chlorine monoxide and the interaction of ozone

and chlorine occur at nearly the same velocity in carbon tetrachloride solution as in the gaseous state. Similarly the combinations of triethylamine and ethyl iodide and of acetic anhydride and ethyl alcohol take place at the same velocity in solution as in the gas phase (*cf.* Hinshelwood, *Ann. Rep. Chem. Soc.*, 1932, p. 43).

The absorption measurements of the solutions of organic acids carried on by Ghosh and co-workers show that oxalic acid has greater absorption in the near ultraviolet and it is well known that oxalic acid decomposes more readily in the same region.

Kailan (*Monatsh.*, 1913, **34**, 1209) has found that when 0·5 to $2N$ solutions of acetic, oxalic, malonic, succinic, malic and tartaric acids are exposed to ultraviolet light from a quartz lamp, slight decomposition takes place. In recent communications Dhar and Atma Ram (*J. Indian Chem. Soc.*, 1933, **10**, 287) and Dhar and Bhargava (*Nature*, 1933, **132**, 30) have shown that aqueous solutions of organic acids decompose even in sunlight and the decomposition is accelerated in presence of oxygen. The decomposition velocity increases with the introduction of an alcoholic hydroxyl group in the molecule. Ferric and uranyl salts and also mercuric chloride accelerate these decompositions. Moreover, the researches of Ghosh and his collaborators show that the addition of uranium nitrate, ferric chloride or mercuric chloride markedly increases the light absorption of these organic acids. Here again we find that the weakening of the binding forces of molecules is associated with increased light absorption.

In publications from these laboratories we have shown that the oxidation of several organic acids by chromic acid or potassium permanganate is markedly accelerated by manganese salts and that these reactions are increased in light. We have made careful measurements of absorption spectra of the mixtures of organic acids with chromic acid or potassium permanganate, with or without the addition of manganese sulphate and we have observed that in all cases addition of manganese sulphate markedly increases the light absorption.

It has already been stated that the predissociation limit of benzaldehyde is 2550Å. De Hemptinne (*J. Phys. Radium*, 1928, *vi*, **9**, 357) has shown that the photolysis of benzaldehyde by radiations shorter than 2600Å takes place as follows:

$$C_6H_5CHO = C_6H_5 + H + CO$$

The hydrogen reacts with the phenyl group to form benzene. The energy necessary for this decomposition is calculated to be 115780 cal corresponding to radiations of wave-length 2461Å. This is the wave-length at which the total absorption band of benzaldehyde spectrum begins. Between 400-500° benzaldehyde decomposes thermally. The decrease in the light energy necessary for decomposition at the higher temperatures is of the same order of magnitude as the increase in the vibrational energy of the benzaldehyde molecule as calculated from the variation in the specific heat with temperature. On the other hand in presence of oxygen, benzaldehyde undergoes oxidation even in the dark and rapidly in visible light. Bäckström (*J. Amer. Chem. Soc.*, 1929, **51**, 90) has shown that in the photo-oxidation of benzaldehyde in radiations of wave-lengths 3660-2536Å a very large quantum yield is obtained. Similarly Haber and Wansbrough-Jones (*Z. physikal. Chem.*, 1932, **B**, **18**, 103) have reported that a solution of sodium sulphite produces hydrogen in only short ultraviolet light. In presence of oxygen, however, the sodium sulphite undergoes chemical change in the dark and markedly in light with an abnormally high quantum yield. Moreover, the photo-decompositions of iodoform, chloroform, ethyl iodide, methyl iodide, hydroiodic acid, etc., are greatly accelerated in presence of oxygen. All these results show that increase in chemical reactivity is always associated with light absorption.

From the foregoing discussion it will be evident that the controversy regarding the minimum frequency of radiations capable of initiating the chlorine—hydrogen reaction loses much of its significance because in presence of hydrogen the Cl—Cl linking is weakened and hence radiations of wave-lengths greater than 5000Å, which are the limit of sensitised decomposition of chlorine molecules, can initiate the chemical change. With numerous photochemical reactions involving molecules of chlorine, bromine or iodine we have observed that radiations of wave-lengths 7804, 8500 and 8700Å are capable of initiating these reactions with halogens and reducing agents This happens because due to the presence of reducing agents, the binding forces of the halogen molecules are considerably weakened and they are readily broken up either by increase of temperature or illumination and in many cases, increased light absorption has been observed with the mixtures. Hence the reactivity of a mixture is preceded by the formation of an additive product with weakening

of the binding forces and increased light absorption. It has been postulated that in the photochemical reactions involving the halogens, the primary change is the atomisation of the halogen molecules but the foregoing discussion shows that the first stage is the formation of an additive compound, may be of an unstable nature having an increased light absorption and this leads to the weakening of the binding forces of the halogen molecules.

In a recent communication Bhattacharyya and Dhar (*Z. anorg. Chem.*, 1932, **209**, 128) have shown that $N/10$ solutions of trichloroacetic acid decomposes at 45° or higher temperatures in radiations of wave-lengths 6235, 4700, 4000, 3840, 3536, 3621, 3125Å. The reaction in the dark at 60° is exceedingly slow. The velocity of the reaction in ultraviolet light is much greater than in visible light. From measurements on light absorption of aqueous solutions of trichloroacetic acid it is seen that there is appreciable absorption in the visible spectrum but the absorption is greatly increased in the ultraviolet, where marked absorption begins from 3200Å and complete absorption from 3100. The dissociation energies of the linkings C—Cl, C—Br, C—I are 78·2, 60, 42·8 cal respectively. It is not definitely known whether C—Cl or C—O or O—H link is broken when tricholoracetic acid is illuminated but it is quite certain that ultraviolet radiation is necessary to break these links. As the experimental results show that trichloroacetic acid solutions are decomposed even by visible light, it appears that in presence of water, the above links are weakened and the whole reaction appears to be photosensitised by the presence of water.

Recently, Bowen and Tietz (*J. Chem. Soc.*, 1930, 234) have observed that the photo-oxidation of acetaldehyde, when dissolved in water by oxygen, is greater than in the gaseous state. Hence again the C=O or O—H link seems to be weakened by the presence of water. Moreover, it is well known that peroxides, which are addition products of the reacting aldehydes with oxygen are at first formed when aldehydes are brought in contact with oxygen.

It was generally believed that several bimolecular thermal reactions taking place in solution possessed velocities smaller than those calculated according to the expression (number of collisions) $\times e^{-E/RT}$.

This expression can predict the correct order of magnitude of numerous gaseous reactions depending on collisions. It has now been observed that there are several reactions in solution in which

the velocities are in agreement with the calculated values but there are other reactions in the dissolved state in which the observed velocity is much greater than the calculated one (*cf*. Moelwyn-Hughes, *Phil. Mag.*, 1932, *vii*, **14**, 112). These are cases of sensitisation in presenee of water. It is well known that many chemical changes are accelerated by the presence of moisture. Dhar (*Z. anorg. Chem.*, 1926, **159**, 103) has suggested that in many photochemical reactions a cluster containing an ion and the reacting substances is formed in presence of moisture. Lewis (*Nature*, 1928, **121**, 792) has reported that clustering takes place in the photochemical decomposition of nitrous oxide. Recently Forbes and collaborators (*J. Amer. Chem. Soc.*, 1933, **55**, 588) have advanced the view that photochemically efficient clusters are formed in the photo-oxidation of quinine by chromic acid in presence of sulphuric acid.

Kistiakowsky (*J. Amer. Chem. Soc.*, 1927, **49**, 2194) has reported that intensive drying of chlorine gas does not effect its light absorption. The experimental observations of Rodebush and Klingelhofer (*Proc. Nat. Acad. Sci.*, 1932, **18**, 531) and Allmand and Craggs (*Nature*, 1932, **130**, 927) seem to show that drying causes no inhibition of the chlorine—hydrogen reaction.

In recent years the existence of free OH radical as an intermediate product has been assumed by numerous workers in many chemical reactions and flames.* Moreover, it has been postulated that in the reaction of hydrogen atoms with oxygen molecules, the first stage consists of an associative reaction between these atoms and oxygen molecules (*cf*. Bates and Lavin, *J. Amer. Chem. Soc.*, 1933, **55**, 81).

$$H + O_2 \longrightarrow HO_2$$

It is of interest to note that OH radical possesses many absorption lines in its spectrum in the region 3080 to 3267Å whilst hydrogen and oxygen show no absorption in this region. Further work in this line is in progress in this laboratory.

Summary.

1. From recent researches on photo-dissociation and predissociation, it can be concluded that in general, an increase in the light absorption by a molecule is associated with its increased chemical reactivity and weakening of the binding forces and conversely when

a molecule becomes more reactive, it is likely to absorb light more markedly.

2. Increase of temperature enhances the amount of light absorption and activity of the molecule and it decomposes on illumination by radiations of longer wave-lengths.

3. The presence of hydrogen sensitises the dissociation of chlorine molecules and makes them reactive in radiations of longer wave-lengths.

4. The addition of an oxalate markedly sensitises the decomposition of molecules of iodine and they are activated in the dark and in radiations of longer wave-lengths. The absorption of light by a solution of an oxalate is appreciably increased by the addition of dilute iodine solution.

5. In presence of uranium nitrate, ferric chloride or mercuric chloride, the light absorption and photo-decomposition of organic acids are greatly increased.

6. When manganese salts are added, the light absorption by mixtures of organic acids and chromic acid or potassium permanganate is increased and the oxidation of the organic acids by chromic acid or potassium permanganate is accelerated by the addition of manganese salts.

7. In presence of reducing agents like hydrogen, carbon monoxide, ferrous salts, nitrite, hydroxylamine, hydrazine, alcohols, acetone, organic acids and their salts, etc., the halogen molecules become reactive even in the dark and in radiations of wave-lengths longer than those necessary for their sensitised or photochemical dissociation, because the binding forces of the halogen molecules are considerably weakened due to the reducing agents.

8. The presence of water may sensitise the photo-decomposition of some substances by weakening the binding forces and increasing the light absorption.

9. It appears that the first stage in a reaction between two or more molecules, is the formation of an additive product with weakening of the linkages and increased light absorption. This is likely to happen in thermal as well as in photochemical reactions.

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Condition of Silver Chromate, Silver Iodide and Lead Iodide in Gelatine.

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When one considers the various theories that have been put forward by different investigators to explain the formation of Liesegang rings, it becomes quite clear that a knowledge about the condition—ionic, colloidal, etc., of the substances deposited in the bands will be of great help in understanding the process of periodic precipitation.

Williams and Mackenzie (*J. Chem. Soc.*, 1920, **117**, 844), Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **22**, 162; 1928, **24**, 50) and Bolam and Donaldson (*ibid.*, 1933, **29**, 864) have shown by *e. m. f.* and conductivity measurements that prior to the appearance of the red colour, the activity of the silver ion in the yellow mixture is very much higher than in a pure saturated solution of silver chromate at the same temperature, and that when the red colour appears the activity of the silver ion simultaneously decreases to a marked extent. Desai and Nabar (*Trans. Faraday Soc.*, 1932, **28**, 449) have shown from electrometric measurements that the activity of silver ion in a mixture of silver nitrate and potassium chromate in gelatine remains constant for some minutes, then rapidly decreases and finally becomes constant, and that the point at which the activity commences to fall corresponds in every case with the first appearance of red colour. These experiments lead to the conclusion that the yellow mixture contains silver chromate in supersaturated solution and that the red colour is due to the actual formation of the solid phase, and not to the coagulation of a solid phase which is already present in the form of colloidal particles.

Dhar and collaborators (*J. Phys. Chem.*, 1924, **28**, 41; *Kolloid Z.*, 1924, **34**, 270; *J. Indian Chem. Soc.*, 1928, **5**, 175; *Trans. Faraday Soc.*, 1927, **23**, 28) have, on the other hand, shown from their electrometric and conductivity measurements that silver chromate is produced in the form of a colloidal solution. According

to them, the yellow mixture contains particles which are negatively charged through adsorption of chromate ions, while the red substance is a less stable sol containing particles which are positively charged through adsorption of silver ions. They have shown that a greater part of silver chromate in gelatine is present in colloidal condition, only about one-third being present in ionic condition. It is difficult to understand why the results of various investigators on the condition of silver chromate in gelatine are so conflicting.

Chatterji and Dhar (*J. Indian Chem. Soc.*, 1930, 7, 177) have shown from *e.m.f.* and conductivity measurements that more than 97% of silver iodide in gelatine exists in condition other than ionic; they believe that it is present in colloidal condition.

Desai and Naik (Paper on "Inhibitive power of Gelatine" which will be published in the September issue of the Journal of the Bombay University, 1933) have shown that the inhibitive power with reference to Ag_2CrO_4 is minimum for gelatine of p_H 5·75 and is greater for higher or lower values of p_H. In the case of AgI the inhibitive power continuously decreases with a decrease of p_H of gelatine. The inhibitive power with reference to PbI_2 is maximum for gelatine of p_H 5·0 and is smaller for higher or lower values of p_H.

Condition of Silver Chromate in Gelatine.

If yellow solution contains silver chromate in supersaturated solution and not in colloidal condition, one would expect that the conductivity of the yellow mixture should remain the same as that calculated on the basis that all silver chromate exists in ionic condition as long as the colour does not change and that it should gradually decrease with the appearance of the red coloured precipitate. To test this point, a series of conductivity experiments were also undertaken.

The gelatine used in these experiments was the same as used by Desai and Naik (*loc. cit.*) and the p_H of gelatine solution was varied in the same manner as done by them. The conductivity was measured by the usual method using an amplifying circuit similar to the one used by Lorenz and Klauer (*Z. anorg. Chem.*, 1924, 136, 121) (for details please see paper by H. N. Desai, D. B. Naik and B. N. Desai on conductivity measurements in course of publication in *Indian J. Phys.*). The conductivity of the mixture was determined

from time to time. A typical result of conductivity experiments is given in Table I. In Table II is given a summary of all such results obtained with silver chromate.

TABLE I.

Total volume of mixture with conductivity water = 20 c.c. Conc. of gelatine soln. = 3%. pH of gelatine soln. = 5·52. A. Conductivity of 5·5 c.c. gelatine + water = $1·855 \times 10^{-4}$. B. Conductivity of 5·5 c.c gelatine + 5 c.c. $N/100$-$AgNO_3$ + water = $4·547 \times 10^{-4}$. C. Conductivity of 5·5 c.c. gelatine + 5 c.c. $N/100$-K_2CrO_4 + water = $4·579 \times 10^{-4}$. D. Conductivity of 5·5 c.c. gelatine + 5 c.c. $N/100$-KNO_3 + water = $4·926 \times 10^{-4}$ Temp. = 30°.

Colour of mixture.	Time.	Obs. conductivity (mhos) of mixture 5·5 c.c. gelatine + 5 c.c. $N/100$-$AgNO_3$ + 5 c.c. $N/100$-K_2CrO_4 + water. E.	Obs. conductivity (mhos) of Ag_2CrO_4 alone. E—D.	Calc. conductivity (mhos) if whole of Ag_2CrO_4 in ionic condition. B + C—D—A.	% of Ag_2CrO_4 in ionic condition.
Yellow	1 min.	$6·842 \times 10^{-4}$	$1·916 \times 10^{-4}$	2·845 × 10	67
,,	6	6·842	1·916		67
,,	10	6·798	1·872		66
,,	15	6·842	1·916		67
,,	20	6·821	1·895		67
,,	25	6·798	1·872		66
,,	30	6·821	1·895		67
,,	35	6·842	1·916		67
,,	40	6·842	1·916		67
,,	45	6·798	1·872		66
,,	50	6·821	1·895		67
,,	55	6·842	1·916		67
First appearance of red colour.	59	6·842	1·916		67
Red	65	6·798	1·872		66
,,	70	6·842	1·916		67
,,	75	6·821	1·895		67

TABLE II.

Temp. = 30°. Total volume = 20 c.c.

pH of gelatine.	Vol. of gelatine.	$N/100$-$AgNO_3$ and $N/100$-K_2CrO_4.	Obs. conductivity (mhos) of Ag_2CrO_4 alone in mixture.	Calc. conductivity (mhos) if whole of Ag_2CrO_4 in ionic condition.	% of Ag_2CrO_4 in ionic condition.
			B−D.	B+C−D−A.	
5·52	5·5 c.c.	5 c.c.	$1·895 \times 10^{-4}$	$2·845 \times 10^{-4}$	67
5·52	2·8	4	1·239	1·978	62
5·52	5·0	5	1·260	2·268	56
5·52	6·0	6	1·126	2·576	44
5·52	7·0	6	1·130	2·592	44
4·50	1·25	6	1·889	3·685	51
4·50	1·3	5	1·670	2·561	65
6·00	7·2	6	1·210	2·850	43

It will appear from Table I that when equivalent amounts of $AgNO_3$ and K_2CrO_4 are added to the same amount of gelatine, the conductivity is slightly less in the former case than in the latter. This is probably due to the fact that more of Ag ions than CrO_4 ions combine with gelatine (*cf.* Bolam and Mackenzie, *loc. cit.*). It will also be seen that the conductivity is reduced more in the presence of K_2CrO_4 than in the presence of an equivalent amount of KNO_3. This will mean that there is greater combination between gelatine and CrO_4 ions than between gelatine and NO_3 ions. An exactly similar behaviour is noticed in all the cases whether p_H of gelatine is made smaller or larger than 5·52.

The other and most significant fact noticeable from Table I is that no sooner the solutions are mixed, the conductivity is immediately reduced and thereafter its value does not change even when the red coloured precipitate makes its appearance. Also there is no gradual decrease in the conductivity with the appearance of more and more red coloured precipitate. Whatever changes are to take place in the conductivity occur immediately on mixing the solutions. The same behaviour is noticed when the p_H of gelatine

solution is made smaller or larger than 5·52 or when the amount of gelatine is varied keeping the amount of the reactants the same. These results therefore show that (*i*) the yellow coloured mixture contains some insoluble precipitate of silver chromate and (*ii*) that the change from the yellow coloured mixture to the red coloured one is not due to release of supersaturation. From the cataphoretic experiments, it is seen that neither the yellow nor red coloured mixture contains any charged particles. It thus appears that the change from the yellow coloured to red coloured mixture is not due to a change in the charge on the particles of the insoluble precipitate formed in the beginning, but simply due to a change in the size of the particles. One can actually see that the particles are invisible in the yellow mixture, while they are sufficiently large to be visible in red coloured mixture. It was also observed that when the reaction is allowed to take place in test tubes and specially when the mixture sets to a gel, the precipitate is first localised at certain points and the mixture ultimately becomes turbid red. A change in the colour due to a change in the size of particles is a very common phenomenon, for example gold sol containing fine particles is ruby red while the one containing larger particles is blue ; one can quote many such instances. It appears that the yellow mixture contains some insoluble precipitate of silver chromate whose particles are in a highly dispersed form, probably even in molecular condition. If the precipitation is molecularly dispersed, it is quite likely that this portion will diffuse at an appreciable rate. This process of diffusion may give rise to union of groups of molecules which may form centres of crystallisation. More of the molecularly dispersed material will, as a result of diffusion, allow the nuclei already formed to grow and thus larger particles, which may be quite visible will, appear. Growth of larger particles at the expense of smaller particles is thus not at all impossible or precluded. The transition from the yellow to red colour will thus be gradual, but in actual practice is noticed only when red coloured fine particles appear.

It will also be seen from Table I that in this particular case about 67% of silver chromate remains in ionic condition and the remaining 33% in a finely dispersed condition in the yellow mixture. As stated before, the colour change from yellow to red does not seem to be due to a sudden release of supersaturation or due to a change in the nature of charge on the colloidal particles.

In all the cases given in Table II, it was also noticed that whatever changes in the conductivity are to take place, occur immediately on mixing the solutions and that the change from the yellow to the red colour is not accompanied by any changes in conductivity. These results, therefore, apparently support the observations of Chatterji (*Proc. Indian Science Congress*, 1932, p. 10) that the *e. m. f.* does not decrease with time with either yellow or red mixtures. It is surprising that the present results do not support either our previous results (Desai and Nabar, *loc. cit.*) or those of Bolam and co-workers (*loc. cit.*). It is, however, a fact that both types of results are based on accurate experiments. Therefore some more work is necessary to find out the conditions favourable for the occurrence of the different behaviours noticed so far.

It will also appear from Table II that by varying the p_H and the concentration of gelatine and of the reactants, the amount of silver chromate which can remain in ionic condition can also be varied ; in the present case it has varied from 48 to 67%. In view of this, it is not impossible that under certain circumstances the amount of silver chromate which can remain in ionic condition can be as much as 95% (Nabar and Desai; *Nature*, 1931, 127, 628). It is quite likely that the same causes which are operative in this case might also be responsible for the conflicting results discussed in the previous paragraph. We are of the opinion that if the p_H of gelatine and the concentration of gelatine and of the reactants are such that on mixing the solutions more than 95% of silver chromate can remain in ionic condition, on allowing the mixture to stand the *e. m. f.* or conductivity may not change at all till the colour remains yellow (as observed by Bolam and co-workers, *loc. cit.*, and by Desai and Nabar, *loc. cit.*) and that with the appearance of red colour, the *e. m. f.* and conductivity may change gradually ; in such a case the colour change will be due to release of supersaturation. This point is being investigated.

Condition of Silver Iodide in Gelatine.

A typical result of conductivity measurements of silver iodide is given in Table III and a summary of all such results in Table IV

TABLE III.

Temp. = 30°. Total volume with conductivity water = 20 c.c. Conc. of gelatine soln. used = 3%. p_H of gelatine soln. = 5·52. A. Conductivity of 12 c.c. gelatine + water $= 2·746 \times 10^{-4}$ mhos. B. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10$-$AgNO_3$ + water $= 1·981 \times 10^{-3}$ mhos. C. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10$-KI + water $= 2·201 \times 10^{-3}$ mhos. D. Conductivity of 12 c.c. gelatine + 3 c.c. $N/10$-KNO_3 + water $= 2·245 \times 10^{-3}$ mhos.

Colour of mixtures.	Time.	Obs. conductivity (mhos) of mixture 12 c.c. gelatine + 3 c.c. $N/10$-$AgNO_3$ + 3 c.c. $N/10$-KI + water.	Obs. conductivity (mhos) of AgI alone.	Calc. conductivity (mhos) if whole of AgI in ionic condition.	% of AgI in ionic condition.
		E.	E − D.	B + C − D − A.	
Greenish	1 min.	$2·259 \times 10^{-3}$	$0·014 \times 10^{-3}$	$1·662 \times 10^{-3}$	N
	5	2·259	0·014		
	10	2·252	0·007		
	15	2·259	0·014		
	20	2·259	0·014		
Gradual	25	2·245	...		
change	30	2·252	0·007		
	35	2·259	0·014		
	40	2·259	0·014		
	45	2·252	0·007		
Appearance of	50	2·252	0·007		
whitish yellow	55	2·252	0·014		
colour					

TABLE IV.

Temp. = 30°. Total volume = 20 c.c.

p_H of gelatine.	Vol. of gelatine.	$N/100$-$AgNO_3$ and $N/10$-KI.	Obs. conductivity (mhos) of AgI alone in mixture. E − D.	Calc. conductivity (mhos) if whole of AgI in ionic condition. B + C − D − A.	% of AgI in ionic condition.
5·52	2·6 c.c.	1 c.c.	$0·010 \times 10^{-3}$	$0·469 \times 10^{-3}$	2
5·52	5·2	2	0·017	1·080	2
5·52	8·1	3	0·031	1·706	1
5·52	12·0	3	0·014	1·662	nil
4·50	10·0	3	0·018	1·531	1
4·50	12·0	3	0·022	1·774	nil
6·00	7·2	3	0·012	0·947	1

It will appear from Table III that the conductivity of silver nitrate in gelatine is somewhat smaller than that of an equivalent amount of potassium iodide in gelatine. This again indicates as in the previous case that Ag ions combine more readily with gelatine than CrO_4 ions. Also the conductivity is smaller with potassium iodide in gelatine than with an equivalent amount of potassium nitrate in gelatine. Here there is evidence to show that iodide ions combine more readily with gelatine than nitrate ions. A similar tendency is noticeable in all the experiments whose results are summarised in Table IV.

The colour of the mixture becomes greenish on mixing the solutions of $AgNO_3$ in gelatine and KI in gelatine. The mixture, however, does not contain any visible particles. On allowing the mixture to stand, the colour gradually changes and with it the mixture also begins to develop turbidity. With the progress of time, the turbidity continuously increases. It will, however, appear from the table that the conductivity changes immediately on mixing the solutions and that it does not change at all thereafter although the colour of the mixture continuously changes and the particles of silver iodide become visible and gradually increase in size. These results therefore show that colour changes are not due to any release of supersaturation.

It will be seen from Tables III and IV that about 98% of silver iodide exists in condition other than ionic. Our results therefore support the results of Chatterji and Dhar (*loc. cit.*) in this respect. They, however, believe that silver iodide in gelatine exists in colloidal condition. To test this point, a series of cataphoretic experiments were undertaken. In no case the presence of charged particles could be detected. We are therefore inclined to the view that silver iodide in gelatine exists in the beginning in a very highly dispersed form probably in molecular condition. As pointed out before, this portion in molecularly dispersed form will, as a result of diffusion, give rise to large particles and the colour changes are due to changes in the size of the particles. As is well known there is always a tendency for larger particles to grow further at the expense of relatively smaller particles.

A change in the p_H or in the concentrations of gelatine and the reactants does not very appreciably alter the amount of silver iodide in ionic condition. In this respect silver iodide in gelatine is quite distinct from silver chromate in gelatine. In so far as can be

judged from the present results, the fact that the inhibitive power of gelatine decreases with a decrease of its p_H, does not seem to be of any significance in explaining the results about condition of silver iodide in gelatine.

Condition of Lead Iodide in Gelatine.

A typical result of changes in the conductivity with time in the case of lead iodide in gelatine is given in Table V. A summary of all such experiments is also given in Table VI.

TABLE V.

Temp. = 30°. Total volume with conductivity water = 20 c.c. Conc. of gelatine soln. = 3%. p_H of gelatine = 5·52. A. Conductivity of 9 c.c. gelatine + water = 2·096 $\times 10^{-4}$ mhos. B. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-Pb $(NO_3)_2$ + water = 1·022 $\times 10^{-3}$ mhos. C. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-KI + water = 1·479 $\times 10^{-3}$ mhos. D. Conductivity of 9 c.c. gelatine + 2 c.c. $N/10$-KNO_3 + water = 1·683 $\times 10^{-3}$ mhos.

Colour of mixture.	Time (hrs. min.).	Observed conductivity (mhos) of mixture 9 c.c. gelatine + 2 c.c. $N/10$-Pb $(NO_3)_2$ + 2 c.c. $N/10$-KI + warer. E.	Observed conductivity (mhos) of PbI_2 alone. E−D.	Calculated conductivity (mhos) if whole of PbI_2 in ionic condition. B+C−D−A.	% of PbI_2 in ionic condition.
Colourless	0·01 hr.	2·187 $\times 10^{-3}$	0·504 $\times 10^{-3}$	0·608 $\times 10^{-3}$	83
	0·30	2·179	0·496		82
	0·45	2·187	0 504		83
	1·00	2·179	0·496		82
	1·15	2·184	0·501		82
	1·30	2·173	0·490		81
	1·45	2·187	0·504		83
Gradual	2·00	2·179	0·496		82
change	2·30	2·187	0·504		83
	3·00	2·179	0·496		82
	3·30	2·184	0·501		82
	4·00	2·173	0·490		81
	4·30	2·187	0·504		83
Apparance of	4·50	2·179	0·496		82
greenish colour	5·00	2·179	0 496		82
Gradual	5·45	2·187	0·504		83
change	6·30	2·179	0·496		82
Appearance of yellow colour	8·30	2·184	0 501		82

TABLE VI.

Temp. = 30°. Total volume = 20 c.c.

p_H of gelatine.	vol of $N/10$-$Pb(NO_3)_2$ gelatine.	and $N/10$-KI	Observed conductivity (mhos) of PbI_2 alone in mixture.	Calculated conductivity (mhos) if whole of PbI_2 in ionic condition.	% of PbI_2 in ionic condition.
			E−D	B+C−D−A	
5·52	5·6c.c.	2·0 c.c.	$0{\cdot}586 \times 10^{-3}$	$0{\cdot}761 \times 10^{-3}$	76
5·52	12·6	2·5	0·680	0·960	65
5·52	9·0	2·0	0·501	0·608	82
4·50	13·2	2·5	0·554	0·819	68
4·50	10·0	2·0	0·511	0·616	83

A well marked tendency for the combination of lead ions with gelatine is noticeable from the results given in Table V, for it is observed that the conductivity with lead nitrate is less than th with an equivalent amount of potassium iodide. These re also support the conclusion arrived at in the case of silver in gelatine, namely that iodide ions combine more readily gelatine than nitrate ions.

When lead nitrate in gelatine is mixed with potassium iodide in gelatine, the mixture is colourless. On allowing the mixture to stand, however, a colour develops which gradually changes from greenish to yellow. Simultaneously with these colour changes the mixture which is quite clear in the beginning develops turbidity and gradually the size of the particles also increases. However as in the case of silver chromate and silver iodide in gelatine, the colour changes are not due to any release of supersaturation, for whatever changes are to take place in the conductivity of the mixture occur immediately on mixing the solutions of lead nitrate and potassium iodide in gelatine. The conductivity also does not change at all with time. The cataphoretic experiments showed that at no stage the particles of lead iodide in gelatine are charged and it therefore appears to us that the insoluble portion of lead iodide in gelatine exists in a very highly dispersed condition as in the case of insoluble portion of silver chromate and of silver iodide in gelatine. In this case also the colour changes might be due to changes in the size of the particles.

It will appear from Table V that in this particular case about 40% of lead iodide exists in a finely dispersed condition and the remaining 60% in ionic condition. It is also noticed from Table VI that the amount of lead iodide which can remain in ionic condition in gelatine varies from (65% to 83%) with its p_H as well as with a change in the concentration of gelatine and of the reactants. Lead iodide thus behaves exactly as silver chromate in these respects. The present results however do not show if the fact that the inhibitive power of gelatine with reference to [illegible] iodide is maximum for p_H value 5·00 has any significance in [illegible]ining the results about condition of lead iodide in gelatine. [illegible]olam (*Trans. Faraday Soc.*, 1928, **24**, 463; 1930, **26**, 133) has [illegible]me to the conclusion on the basis of conductivity and *e. m. f.* measurements that lead iodide is maintained in a highly supersaturated solution in agar gel. Chatterji and Dhar (*loc. cit.*) have discussed these results of Bolam and shown that the percentage of lead iodide in the ionic state decreases (from 99·8 to 52) as the concentration of lead iodide increases. We are of the opinion that this case is similar to the case of silver chromate and lead iodide in gelatine and the influence discussed under silver chromate (last para, under condition of Ag_2CrO_4) might also be responsible for these conflicting results. It thus seems necessary to investigate further these cases in a greater detail in order to get a correct idea about the condition of these substances in gel.

It will not be out of place to discuss here the meaning of the term "inhibition" as used by various investigators.

We (Desai and Naik, *loc. cit.*) have observed that gelatine of p_H 5·75 has the smallest inhibitive power with reference to Ag_2CrO_4. According to Bolam and Donaldson (*loc. cit.*), the degree of supersaturation and therefore the inhibitive action of gelatine, probably, has an optimum value at p_H 5·0.

This conclusion of theirs is, however, difficult to reconcile with the inferences that can be drawn from Fig. 1 of their paper (*cf.* Bolam and Mackenzie, *loc. cit.*) as well as with our results namely that gelatine of p_H 5·75 has the smallest inhibitive power. If inhibition gives rise to supersaturation, one would have expected least supersaturation for gelatine of p_H 5·75 and greater for gelatine solutions of higher or lower p_H than 5·75. The results of Bolam and Donaldson however do not support this view. It thus appears

that the inhibition experiments (inhibition in the sense of power to prevent precipitation) cannot always be utilised to give an idea of the degree of supersaturation although they may do so in some cases and under certain circumstances. A highly supersaturated solution can only be produced if by some means the formation or the growth of crystallisation centres is prevented. If inhibition gives rise to a colloidal solution (Dhar and co-workers, *loc. cit.*), one would expect that the stability of the yellow sol containing negatively charged particles of Ag_2CrO_4 should regularly decrease with an increase of acidity of gelatine and therefore more and more of gelatine should be required for inhibition with a decrease of p_H; our results however do not completely support the view for the inhibitive power of gelatine of p_H 5·76 to be minimum. Gelatine as an agent preventing precipitation of sparingly soluble substances generally (as in the case of Ag_2CrO_4, AgI and PbI_2), can possibly function as producing either supersaturation or a colloidal solution by preventing aggregation of small particles to larger masses or particles in a very highly dispersed form or two of these three forms or even all the three forms simultaneously Hedges ("Liesegang rings and other periodic structures" 1932, p. 62) has pointed out "it seems, on the whole, that sparingly soluble substances readily form relatively stable, highly supersaturated solutions in gels.......... The formation of colloidal solutions is not ruled out, however, for such a system would probably be produced by a sudden release of supersaturation through some cause or other, just as relatively large crystals would be formed as a result of very slow release of supersaturation". To this one may also add a third possibilty namely that gels may help in producing the sparingly soluble substances in a very highly dispersed form probably in molecular condition and that the union of these very fine particles by diffusion may ultimately give rise to larger visible particles. It thus appears necessary to investigate this problem further in order to understand clearly the difference in the rôle of gelatine in producing supersaturation and in preventing the precipitation of sparingly soluble substances and giving rise to colloidal solutions or in producing particles in a very highly dispersed form In view of the conflicting results about the condition of silver chromate in gelatine, it is necessary to use the term "inhibition" in all cases of prevention of precipitation of sparingly soluble substances whether due to production of either supersaturation or a colloidal solution or particles having a very high

degree of dispersion or any two of the three or even all the three forms simultaneously instead of using that term to indicate only supersaturation as done by Bolam and Mackenzie (*loc. cit.*), Bolam and Desai (*Trans. Faraday Soc.*, 1928, **24**, 50), Bolam and Donaldson (*loc. cit.*) and Desai and Nabar (*loc. cit.*, *cf.* also *J. Indian Chem. Soc.*, 1932, **9**, 141; *J. University of Bombay*, 1932, **1**, Part II, 28).

SUMMARY.

1. Experiments have been carried out to determine the condition of silver chromate, silver iodide and lead iodide in gelatine.

2. The conductivity results show that whatever changes in the conductivity are to take place occur immediately on mixing the solutions and that there is no gradual decrease of conductivity with changes in colour of the mixtures. The cataphoretic experiments do not show the presence of any charged colloidal particles in any of the cases. These results suggest that immediately the solutions are mixed some insoluble precipitate is produced, the particles of which are in a very highly dispersed condition—probably in molecular condition—and that changes in the colour of the mixtures are due to growth of these very fine particles into larger ones. A suggestion is made as to the likely causes of the conflicting results about the condition of silver chromate in gelatine.

3. The amount of silver chromate and lead iodide in ionic and highly dispersed condition varies to a large extent, depending on the p_H of gelatine and the concentration of gelatine and of the reactants, silver iodide does not show such a behaviour.

4. There is evidence to show that the tendency for the combination of various ions with gelatine is in the order $\begin{cases} Ag > CrO_4 > NO_3 \\ Ag > I > NO_3 \\ Pb > I > NO_3. \end{cases}$

5. It is pointed out that the term "inhibition" should be used to indicate power to prevent precipitation generally whether it may be due to production of supersaturated solution or of colloidal solution or of particles in a very highly dispersed condition.

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Influence of Acidity of Gelatine on the Liesegang Rings of Silver Chromate and Silver Iodide.

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Desai and Nabar (*J. Indian Chem. Soc*, 1932, **9**, 141) have studied the changes in the nature of rings of silver chromate in gelatine when the acidity of the latter is increased. They have observed that an increase in the acidity of gelatine is accompanied by a decrease (*i*) in the time after which the first ring appears, (*ii*) in the distance between the same successive rings, and (*iii*) in the number of rings that can be obtained. While discussing their results they have suggested that there might be definite limits to the p_H value of gelatine within which good rings of silver chromate can be obtained. The present work was undertaken with a view to test this suggestion by obtaining rings of silver chromate in gelatine whose p_H is varied over a wide range and also to see if the variation of p_H has any influence on the nature of rings of silver iodide in gelatine. The sample of gelatine used in these experiments was the same as used by Desai and Naik (Paper on "Inhibitive power of gelatine" which will be published in the September issue of the Journal of the Bombay University, 1933) and the p_H of gelatine solution was varied in the same manner as done by them.

Rings of Silver Chromate in Gelatine.

1·5 C.c. of a normal solution of silver nitrate were allowed to diffuse into 20 c. c. of a 20 % gelatine gel impregnated with 0 9 c.c. of a normal solution of potassium chromate. The test tubes used in these experiments were all of the same diameter. The experiments were carried out in a room whose temperature (30°) did not appreciably fluctuate during the day. The distances between successive rings were measured by means of a cathetometer. The results are summarised below.

(1) Maximum number of rings are obtained with samples of gelatine having p_H 5·25 and 5·00 and their number decreases in gels of higher or lower p_H than this range.

(2) The distances between successive rings increase with all samples of gelatine. The distances between the same successive rings are greatest for gelatine of p_H 5·75 and smaller for samples of gelatine of p_H higher or lower than 5·75.

(3) Rings appear early in acidified gelatine while their appearance is delayed in samples whose acidity has been decreased. In conformity with this, the distance of the first ring from the top increases with an inrease of p_H.

The following observations were also made during this work.

(4) There is a tendency to get spiral shaped or broken rings in samples of acidified gelatine and larger and larger crystals are obtained with an increase of acidity. In samples of gelatine whose p_H is high, no rings are obtained and the precipitate is found to be more or less uniformly distributed.

(5) The size of the particles in the rings generally increases from the first to the last ring.

FIG. 1

1 2 3 4 5 6 7 8 9 10

$p_H \longrightarrow$ 4 4·25 4·5 4·75 5 5·25 5·5 5·75 6 6·25

In Fig. 1 is given a photograph of rings of silver chromate in samples of gelatine of different p_H. This photograph was taken with transmitted light. It corroborates what has been stated above. In test tube No. 1, one can easily see the presence

of big crystals. The following additional conclusions can be drawn from the photograph.

(6) With an increase in the acidity of gelatine the thickness of the rings decreases.

(7) In any particular sample of gelatine, the thickness of the rings increases from the first ring to the last ring, but its compactness decreases at the same time.

These results support largely the observations of Desai and Nabar (*loc. cit.*). The slight differences in the results are due to changes in the concentration of gelatine and the reactants used in their experiments and in the present investigation. The influence of these factors is being further studied in greater detail.

The present results, however, completely support the suggestion of Desai and Nabar (*loc. cit.*) that there might be a definite range of p_H of gelatine within which good rings of silver chromate can be obtained.

It has been shown by us (Naik, Desai and Desai, *J. Indian Chem. Soc.*, 1934, **11**, 45) that the results about condition of silver chromate in gelatine in the yellow mixture are rather conflicting. It might exist either in supersaturated condition, colloidal condition or in a highly dispersed condition—particles being even of molecular size (*cf.* Naik, Desai and Desai, *loc. cit.*), in any two of the three or even simultaneously in all the three conditions. It is therefore considered advisable not to explain these results of ring experiments until we are able to find out the causes of the conflicting nature of the results of different investigators as well as our own different sets of experiments about the condition of silver chromate in the yellow mixture. It should, however, be stated that these experiments clearly show that samples of gelatine which are slightly acidic give good rings of silver chromate while those which may be relatively more alkaline may not give any rings at all. Also there is a definite range of p_H of gelatine in which good rings of silver chromate can be obtained ; the fact that gelatine with p_H 5·75 (Desai and Naik, *loc. cit.*) shows a minimum inhibitive power seems to have a bearing on the distances *between the same successive rings* (*cf. section* 2 above). Bolam and Donaldson *Trans. Faraday Soc.*, 1933, **29**, 864) have pointed out that the degree of supersaturatian of silver chromate in gelatine increases slightly as the p_H decreases from 5·7 to 5·0, and then falls off more rapidly as

the p_H is further decreased. They have concluded that the degree of supersaturation probably has an optimum value at p_H 6·0 This fact seems to have some bearing on the nature of rings of silver chromate in gelatine, for as shown above best rings are obtained in samples of gelatine of p_H range, 6·0 to 5·25.

Rings of Silver Iodide in Gelatine.

1·5 C.c. of a 20% silver nitrate solution were allowed to diffuse into 20 c.c. of a 20% gelatine gel impregnated with 1 c.c. of a normal solution of potassium iodide. The test tubes were kept in a dark box during the period of formation of rings in order to prevent the effect of light as far as possible. The results of these experiments are summarised below.

(1) All samples of gelatine are equally effective in giving rings of silver iodide. Thirty three rings were obtained in each case.

(2) In all the cases the distances between successive rings first decrease regularly and then increase. The closest rings are those which occur between the eighteenth and the twentythird ring.

(3) The distances between the same successive rings decrease more or less regularly with an increase of the p_H of gelatine.

(4) The first ring appears after about 23 hours in all the cases.

From observation (3) it would appear that for values of p_H much higher than 6·0, only a continuous band of precipitate might be obtained instead of a number of rings. This is rather interesting in view of the fact as shown by Desai and Naik (*loc. cit.*) that the inhibitive power of gelatine with reference to AgI continuously increases with an increase in the p_H of gelatine. It is, however, necessary to carry out more experiments before this fact can be utilised to explain the nature of rings of silver iodide in gelatine.

Silver iodide being relatively very much sensitive to light when compared with silver chromate, it was not found possible to get a good photograph of rings either with transmitted or reflected light. We would however like to record the following visual observations here.

(1) The thickness of the rings is generally much greater than the distance of the clear interspace between the rings.

(2) The thickness of the rings almost regularly decreases from the first ring upto the eighteenth to twentythird ring after which it again begins to increase regularly.

(3) All the rings have got almost the same compactness.

(4) The size of the particles in almost all the rings remains almost the same.

(5) The clear interspace between the first and the eighteenth to twentythird ring became somewhat darkish on exposure to light, while that between the eighteenth to twentythird and the thirtythird ring became deep brown.

According to the various theories that have been put forward to explain the Liesegang phenomena, there should be a gradual increase in the spacing between the successive rings. The fact that the distance between the successive rings of AgI in gelatine decreases up to about the twentieth ring cannot therefore be explained on the basis of any of the existing theories. The other noteworthy instances of this type, *i.e.*, where the distance between the successive rings decreases, are those reported by Davis (*J. Amer. Chem. Soc.*, 1917, **39**, 1312) about bands of mercury obtained by allowing mercurous nitrate to diffuse in agar gel impregnated with sodium formate, by Hedges and Henley (*J. Chem. Soc.*, 1928, 2714) about bands of arsenious sulphide obtained by allowing solutions of ferric chloride or aluminium sulphate to diffuse into agar gel containing sols of arsenious sulphide, and by Mukherjee and Chatterji (*Kolloid Z.*, 1930, **50**, 147) about bands of zinc and nickel ferricyanide and cobalt ferrocyanide. The rings of AgI in gelatine obtained by us are, however, peculiar in this respect that although the distance between successive rings first decreases, it increases in case of the later rings (twentieth to twentythird ring). More detailed work is necessary before these anomalies can be explained.

It has been shown by us (Naik, Desai and Desai, *loc. cit,*) that about, 90% of AgI in gelatine exists in the mixture in condition other than ionic or colloidal. The particles of silver iodide which form on the meeting of $AgNO_3$ and KI are first probably in molecular condition and they grow further due to diffusion . The particles being in a very highly dispersed form, might absorb to a certain extent the substances that may be present in the neighbourhood. However in view of the fact that the space between the rings becomes coloured when exposed to light, it appears that the adsorption may not be very marked.

SUMMARY.

1. Liesegang rings of silver chromate and silver iodide have been obtained in samples of gelatine of different p_H.

2. In the case of silver chromate rings, the results in general support the preliminary results of Desai and Nabar. The suggestion of these authors that there might be a definite range of p_H of gelatine within which good rings of silver chromate can be obtained is also supported by the present results.

3. All samples of gelatine appear to be equally effective in giving rings of silver iodide. The distance between successive rings first decreases and then increases. Also the distances between the same successive rings decrease more or less regularly with an increase of the p_H of gelatine.

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The Photochemical Reduction of Methyl Red by Phenylhydrazine using Chlorophyll Solution as Photosensitiser.

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BöHi (*Helv. Chim. Acta*, 1929 **12**, 121) found that a large number of azo- dyes are reduced by exposure to light in presence of chlorophyll in methyl alcohol solution. The chlorophyll itself is destroyed but this can be prevented by adding one of the following anodic depolarisers: oil of turpentine, piperidine and phenylhydrazine. Addition of the last named compound was found to produce the most rapid photolysis. BöHi did not make any quantitative study and his experimental investigations were based on the theoretical views advanced by Baur (*Z. Electrochem.*, 1928, **34**, 595).

Thus, when the dyestuffs are decolourised by exposure to light and in presence of chlorophyll, the mechanism is as follows:—

$$\text{Chlorophyll}\begin{cases}\oplus\ \text{Chlorophyll} \rightarrow \text{Oxidation products}\\ \ominus\ \text{Dyestuffs} \rightarrow \text{Leuco products}\end{cases}$$

and in presence of anodic depolariser, such as phenylhydrazine, the reaction takes place in the following way:

$$\text{Chlorophyll}\begin{cases}\oplus\ \text{Phenylhydrazine} \rightarrow \text{Oxidation products}\\ \ominus\ \text{Dyestuffs} \rightarrow \text{Leuco products}\end{cases}$$

In this paper, the reduction of the azo-dye, methyl red has been studied in the monochromatic radiations 4358Å and 5460Å.

The paper is divided in four sections. The first section (Sec. A) deals with the reduction of the dyestuff in methyl alcohol solution at 4358 Å. In Sec. B, the same reaction was studied in benzene solution at 4358 Å. The reaction at 5460 Å both in alcohol and benzene

solution, is given in Sec. C. In Sec. D, the reduction of dyestuff by phenylhydrazine hydrochloride is given.

EXPERIMENTAL.

The amount of methyl red reduced was determined by König Marten spectrophotometer. In green region, the methyl red solution obeys Beer's Law. A small rectangular glass cell containing known strength of methyl red solutions in methyl alcohol was placed in spectrometer table and the angles in the disc which gave fields of equal illumination were found out for four or five dilutions. By plotting values of log $tan\theta_2 - \log tan\theta_1$ against the concentration, a straight line was obtained. θ_2 and θ_1 are the final and initial angles respectively. When mixtures of chlorophyll and methyl red were used, a solution of chlorophyll alone of the same concentration was kept in the compensation cell. From the straight line thus obtained the concentrations of methyl red corresponding to any angle could be interpolated easily.

The light source was a point-o-lite mercury arc lamp run from a storage battery of 28 volts and maintained at a constant current of 2·2 amperes. Convex lenses of various focal length placed at a distance from the lamp equal to their focal lengths gave parallel beams of light of different intensities. The reaction vessel $1·55 \times 1·55 \times 0·8$ cm. was made of plane parallel glass sides with a stopper at the top and was placed inside a double jacketted metal box with a plane glass window on one side to admit light. By continuous circulation of water through the annular space in the box from a thermostat by means of a pump, the temperature was maintained constant. Zeiss monochromatic filters which transmit only the radiations of wave-lengths 5460Å and 4358Å in combination with 1 cm. thick dilute copper sulphate solutions were used for green and blue light respectively.

Mercks' indicator methyl red and reagent methanol (free from acetone) were used throughout the experiment. Kahlbaum's reagent phenylhydrazine was purified and stored in the dark in vacuum.

Each reaction is characterised by a long induction period, depending on the strength of oxidant and reductant and intensity of incident light. Generally, it was observed that the induction period decreased with decrease in the concentration of methyl red and increased concentration of phenylhydrazine.

Section A.

TABLE I*a*.

Wave-length = 4358 Å. Solvent = Methyl alcohol. Temp = 25°.

Intensity of radiation absorbed by a solution having initial concentrations $M/10{,}000$-methyl red, $M/20{,}000$-chlorophyll, $M/200$-phenylhydrazine is 196 ergs ; t represents any arbitrary time after the induction period is over.

Time in min.	Conc. of methyl red.	K (zero mol.).
$t+0$	$8·1 \times 10^{-5}$	$0·06 \times 10^{-5}$
$t+30$	6·3	0·058
$t+70$	4·0	

TABLE I*b*.

$3M/20{,}000$-methyl red ...	$t+0$	$t+30$	$t+75$	$t+125$	$t+175$
$M/20{,}000$-chlorophyll ...	15×10^{-5}	$13·2 \times 10^{-5}$	$10·5 \times 10^{-5}$	$7·5 \times 10^{-5}$	$4·5 \times 10^{-5}$
$M/200$-phenylhydrazine ...	$0·06 \times 10^{-5}$	$0·06 \times 10^{-5}$	$0·06 \times 10^{-5}$	$0·06 \times 10^{-5}$	...

The reaction is thus a zero molecular one, equal quantities being converted in equal times, independent of the concentration of methyl red.

Influence of variation of concentration of phenylhydrazine on the velocity of reaction.

TABLE II.

The conditions of experiment are the same as in Table I*a*.

Conc. of phenylhydrazine (mols) ...	0·02	0·01	0·005
$K \times 10^5$ ...	0·055	0·056	0·06

The velocity of reaction is practically independent of concentration of phenylhydrazine.

Influence of concentrations of chlorophyll on the velocity of reaction.

TABLE III.

Intensity of incident radiation = 124 ergs. Initial concentration of the mixture = $M/10{,}000$-methyl red and $M/200$-phenylhydrazine.

Conc. of chlorophyll $\times 10^5$ ...	1·66	2·5	5	10
$K \times 10^5$ ...	0·023	0·027	0·03	0·027

The velocity of reaction passes through a maximum as the concentration of chlorophyll is increased. It has been observed by us that the fluorescent power of chlorophyll also passes through maximum at the same concentration.

Temperature coefficient of the velocity of reaction.—This has been found to be practically unity. The velocity of reaction is independent of temperature within the range of 23° to 35°.

Influence of the state of polarisation of incident radiation.—It has been found that the state of polarisation is without any effect on the velocity of reaction.

Calculation of quantum efficiency.—The energy of radiation was measured by a Moll thermopile and a Moll galvanometer. Radiant energy from a Hefner lamp at a distance of 1 metre from the thermopile whose intensity is equal to 900 ergs produced a deflection of 41 divisions. The light absorbed by a solution 0·8 cm. thick having the composition—$M/10{,}000$-methyl red, $M/20{,}000$-chlorophyll, $M/200$-phenylhydrazine is equivalent to 9 divisions of the galvanometer. Total number of quanta absorbed by the solution exposing a surface of 2·4 sq. cm. $=104\times10^{12}(\lambda=4358\text{Å})$.

The change in concentration of methyl red in 30 minutes $=1{\cdot}8\times10^{-5}$ (*vide* Table I *a*). The volume of reaction vessel $=2{\cdot}4\times0{\cdot}8$ c.c.

Hence the quantum efficiency $\gamma=0{\cdot}13$ approximately.

If however we take into account only the fraction of radiant energy which is absorbed by chlorophyll only, we obtain a much higher quantum yield. Methyl red and phenylhydrazine exposed to blue radiation in absence of chlorophyll does not react with each other. Hence it is clear that the radiant energy absorbed by chlorophyll only is effective. We can as a rough approximation assume that the radiant energy absorbed by chlorophyll molecules in presence of methyl red is given by,

$$I_f=I_a\frac{\epsilon_{chl}\,C_{chl}}{\epsilon_{chl}\,C_{chl}+\epsilon_{meR}\,C_{meR}}$$

where I_a represents the total energy absorbed, ϵ_{chl}, C_{chl}, ϵ_{meR}, C_{meR} represents the molar extinction coefficients and concentrations of chlorophyll and methyl red.

For $\lambda=4358\text{Å}$, $E_{chl}=17{,}000$ and $\epsilon_{meR}=21{,}000$.

Hence the factor $\dfrac{\epsilon_{chl}\,C_{chl}}{\epsilon_{chl}\,C_{chl}+\epsilon_{meR}\,C_{meR}}$ has the value 1/3·4 approximately.

And the real quantum efficiency $\gamma=0{\cdot}45$.

The quantum efficiencies for the experimental data recorded in Table III has been calculated in this way and the results are recorded below.

TABLE IV.

Conc. of chlorophyll $\times 10^5$ ...	1·66	2·5	5	10
γ ..	1·08	0·8	0·45	0·2

Section B.

Dark reaction.—The dark reaction is extremely slow. No change in the concentration of methyl red was observed in 6 hours. A solution containing methyl red, phenylhydrazine and chlorophyll kept in the dark for 20 hours showed only 5 % reduction of methyl red. Hence the velocity of dark reaction can be neglected.

TABLE V.

Intensity of absorbed radiation is 180 ergs when the solution has the following composition: $M/10{,}000$-methyl red, $M/20{,}000$-chlorophyll, $M/50$-phenylhydrazine. $\lambda=4358$ Å. Temp. $=25°$.

Solvent = Benzene.

Time in min.	Conc. of methyl red $\times 10^5$.	$-\frac{1}{C_0}\cdot\frac{dc}{dt}=K$.
$t+0$	4·74	0·0014
$t+120$	4·0	
$t+0$	2·64	
$t+120$	2·24	0·0013

The reaction velocity is too slow to be followed to completion. The agreement between the values of unimolecular constants for different initial concentration of methyl red is, however, quite good.

Effect of varying concentrations of phenylhydrazine.

TABLE VI.

$M/10{,}000$-Methyl red. $M/20{,}000$-Chlorophyll.

Conc. (mols/litre) of phenylhydrazine ...	0·04	0·02	0·01
$K=-\frac{1}{C_0}\cdot\frac{dc}{dt}$	0·0028	0·0014	0·0008

The unimolecular velocity constant with respect to methyl red is proportional to the concentration of phenylhydrazine.

Effect of varying concentration of chlorophyll.

TABLE VII.

$M/10{,}000$-Methyl red. $M/25$-Phenylhydrazine.

Conc. of chlorophyll $\times 10^5$ ...	1·66	5	10
K ...	0·002	0·0028	0·0025

As in the case of methyl alcohol as solvent, the velocity constant is a maximum at the concentration of 5×10^{-5}.

Temperature coefficient.—Temperature has no influence on the velocity constant.

Quantum efficiency.—The quantum efficiency can be calculated from the first data in Table V. $0{\cdot}74 \times 10^{-5}$ g. molecules of methyl red represent the change in concentration in 120 minutes; the total volume of the solution $= 2{\cdot}4 \times 0{\cdot}8$ c.c. The number of quanta absorbed by the solution per second was found to be 70×10^{12}. The number of molecules transformed per sec. $= 1{\cdot}2 \times 10^{12}$. The quantum efficiency $\gamma = 0{\cdot}017$.

If we take into consideration the radiation absorbed by chlorophyll only, γ has the value of 0·05 approximately.

$$\epsilon_{chl} = 17{,}500 \text{ and } \epsilon_{MeR} = 17{,}000.$$

Section C.

TABLE VIII*a*.

Solvent = Alcohol. Temp. = 25°. Incident intensity = 3000 ergs. $M/5{,}000$-Methyl red. $M/25$-Phenylhydrazine. $M/20{,}000$-Chlorophyll.

Time in min. ...	$t+0$	$t+25$	$t+45$	$t+65$
Conc. of methyl red $\times 10^5$ ...	17·46	13·26	9·62	6·0
K (zero) $\times 10^5$ ...	—	0·17	0·18	0·18

TABLE VIII*b*.

Solvent = Benzene. Incident intensity = 1400 ergs. Other conditions same as in Table VIII*a*.

Time in min. ...	$t+0$	$t+30$	$t+90$
Conc. of methyl red $\times 10^5$ ...	11·3	9·5	6·0
$K \times 10^5$ (zero mol.) ...	—	0·06	0·059

TABLE VIIIc.

Conditions same as in Table VIIIb, only the initial concentration of methyl red was less.

Time in min. ...	$t+0$	$t+30$	$t+50$
Conc of methyl red $\times 10^5$	5·8	3·9	2·6
$K \times 10^5$ (zero mol.) ...	—	0·063	0·065

The reaction in both solvents is thus a zero molecular one.

Effect of variation in the concentration of phenylhydrazine in methyl alcohol solution.

TABLE IX.

Conditions same as in Table VIIIa.

Conc. (mols/litre) of phenylhydrazine ...	0·04	0·01	0·005
$K \times 10^5$	0·17	0·18	0·17

The velocity constant is practically independent of the concentration of phenylhydrazine.

Influence of concentration of chlorophyll on velocity constant.

TABLE X.

Incident intensity = 1400 ergs. $M/10{,}000$-Methyl red.
$M/25$-Phenylhydrazine.

Methyl alcohol		Benzene.	
Conc. of chlorophyll $\times 10^5$.	$K \times 10^5$.	Conc. of chlorophyll $\times 10^5$.	$K \times 10^5$.
1·2	0·06	1·66	0·036
2·5	0·077	2·5	0·062
5	0·074	5	0·06
10	0·06	10	0·048

In both these solvents the velocity constant passes through a maximum when the chlorophyll concentration is approximately $2{\cdot}5 \times 10^5$.

Temperature has no influence on the velocity of reaction.

Quantum efficiency.—In both the solvents, the velocity of reaction was found to be proportional to the intensity of incident radiation.

The extinction coefficients for methyl red and chlorophyll in benzene solution for radiation $\lambda = 5460\text{Å}$ are 900 and 1600 respectively. On the assumption that the radiant energy is absorbed by each species of molecules as if the other is not present, we obtain

$$I_{abs} = I_0\left[1 - e^{-\epsilon_{chl}\, C_{chl}} - e^{-\epsilon_{meR}\, C_{meR}}\right]$$

For $C_{chl} = 5 \times 10^{-5}$ and $C_{meR} = 6{\cdot}8 \times 10^{-5}$, $I_{abs.}$ has value $1400 \times 0{\cdot}105 = 147$ ergs. approximately. This agrees well with the value of light absorbed as measured directly by Moll thermopile and galvanometer.

Hence, we are justified in assuming that the light absorbed by chlorophyll only is given by the equation,

$$I = I_0\left[1 - e^{-\epsilon_{chl}\, C_{chl}}\right]$$

In Table VIIIc, light absorbed by chlorophyll alone is 84 ergs. approximately per sq. cm.

Total quantum absorbed per 2·4 sq. cm. $= \dfrac{84 \times 2{\cdot}4}{3{\cdot}6 \times 10^{-12}}$.

Total number of molecules transformed per sec.

$$= \frac{2{\cdot}4 \times 0{\cdot}8 \times 0{\cdot}065 \times 10^{-5} \times 6{\cdot}16 \times 10^{23}}{60 \times 1000}$$

$\gamma = 0{\cdot}24$ approximately. ϵ for chlorophyll in methyl alcohol solution $= 1600$.

The experimental data in Table X have been used to calculate quantum efficiency and the values of γ are recorded below.

TABLE XI.

Methyl alcohol.		Benzene.	
Conc. of chlorophyll $\times 10^5$.	γ.	Conc. of chlorophyll $\times 10^5$.	γ.
1·2	1·0	1·66	0·45
2·5	0·70	2·5	0·48
5	0·32	5	0·24
10	0·13	10	0·10

Section D.

If phenylhydrazine is replaced by phenylhydrazine hydrochloride, the results obtained are materially different. The dark reaction proceeds very slowly though with measurable speed. The dark reaction is found to be unimolecular with respect to each of the reactants.

TABLE XII*a*.

Solvent = Methyl alcohol. Temp. = 30°. Light absorbed by initial reaction mixture at $\lambda = 4358 \text{Å} = 265$ ergs. $M/40{,}000$-Chlorophyll. $M/250$-Phenylhydrazine hydrochloride.

Time in min.	Conc. of methyl red × 10^5.	K (uni mol.).
0	5	
135	4	Induction period.
195	3·35	0·00126
285	2·61	0·00123
305	1·86	0·00123

The velocity of the corresponding dark reaction is given below. The dark reaction has an induction period of about 3 hrs.

TABLE XII*b*.

Time in min.	...	180	300	420
Conc. of methyl red × 10^5	...	5	4·6	4·4
K	...	0·00023		0·00023

Effect of varying concentration of phenylhydrazine hydrochloride.

TABLE XIII.

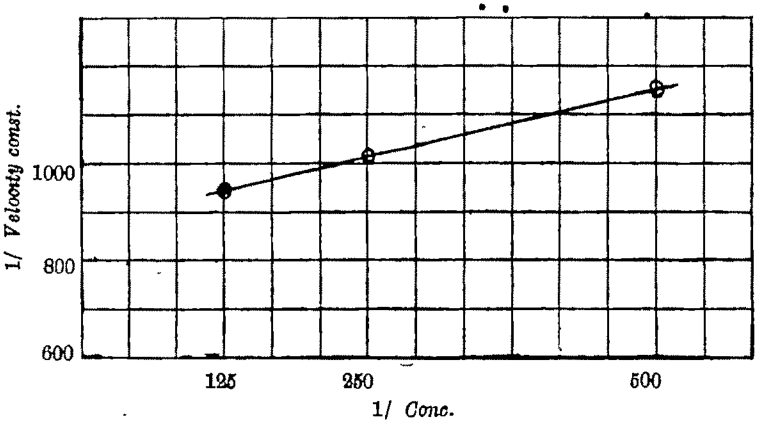
$M/20{,}000$-Methyl red. $M/40{,}000$-Chlorophyll. The incident light same as in Table XII*a*.

Conc. of phenylhydrazine hydrochloride.	K dark & light.	K dark.	K true light.
0·008 M	0·00155	0·0005	0·00105
0·004	0·00123	0·00025	0·00098
0·002	0·00098	0·00012	0·00086

The unimolecular velocity constant for dark reaction is proportional to the concentration of phenylhydrazine hydrochloride, but the velocity of the true light reaction increases slightly as the concentration of phenylhydrazine hydrochloride increases.

I/K plotted against I/C gives a straight line.

FIG. 1.



Effect of variation of concentration of chlorophyll.

TABLE XIV.

$M/20,000$-Methyl red. $M/200$-Phenylhydrazine hydrochloride. Intensity of incident light same as in Table XIIa.

Conc. of chlorophyll.	K (light & dark).	K (dark).	K (true light).
2.5×10^{-5}	0·00120	0·00025	0·00095
10×10^{-5}	0·00140	0·00025	0·00115

The velocity of dark reaction is independent of concentration of chlorophyll, while that of the true light reaction increases slightly as the concentration of chlorophyll increased.

Influence of temperature.—The velocity constant of the dark reaction is approximately doubled by a rise of 10° in temperature while the influence of temperature on the true light reaction is small.

Quantum efficiency.—The quantum efficiency of the reaction is very low; if we take into consideration the whole of the light absorbed by the reaction mixture γ has a value approximately equal to 0·004 and this increases to 0·018 approximately if light absorbed

by chlorophyll alone is considered. Surface of the reaction cell $=4$ sq cm. and the thickness $=0 \cdot 25$ cm.

Similar results were obtained when radiant energy of wave-length 5460 Å is used for bringing about a photochemical change.

TABLE XV.

Radiation absorbed by the solution having composition $M/20{,}000$-methyl red, $M/40{,}000$-chlorophyll, $M/250$-phenylhydrazine hydrochloride $=520$ ergs. Temp. $=30°$. $\lambda=5460$ Å

Time in min. ...	0	50	110	200	320
Conc. of methyl red $\times 10^5$ ...	5	4·5	3·85	3·0	2·1
K(dark & light)	Induction period.		0·00113	0·00110	0·00116
K(true light)	Induction period.		0·00090	0·00087	0·00093

Effect of varying the concentration of phenylhydrazine hydrochloride.

TABLE XVI.

Other condition same as in Table XV.

Conc. (mols/litre) of phenylhydrazine hydrochloride ...	0·004	0·008	0·01
K (true light) ...	0·00085	0·0016	0·00195

The velocity of reaction is proportional to the concentration of phenylhydrazine hydrochloride.

Effect of varying the concentration of chlorophyll.

TABLE XVII.

Other condition same as in Table XV.

Conc. of chlorophyll $\times 10^5$ ...	2·5	5	10
K (true light) ...	0·00085	0·0014	0·0029

Effect of incident radiation on the reaction velocity.—The reaction velocity is found to be directly proportional to the incident intensity. Temperature coefficient is small.

Quantum efficiency.—For $\lambda = 5460 \text{Å}$ and solvent methyl alcohol containing phenylhydrazine hydrochloride, $\epsilon_{chl} = 1800$ and $\epsilon_{meR} = 7600$; in Table XV the total energy absorbed = 520 ergs per sec. per sq. cm.

The energy absorbed by chlorophyll alone equals to 60 ergs approximately. The change in the concentration of methyl red in the last 120 minutes in Table XIIa is $0{\cdot}9 \times 10^{-5}$. The change due to light alone is $0{\cdot}75 \times 10^{-5}$ approximately.

Surface of the reaction cell is 4 sq. cm and the thickness 0·25 cm.

Hence the quantum efficiency $\gamma = 0{\cdot}009$. Since the reaction is unimolecular with respect to methyl red, calculation of quantum efficiency has not much significance except as an indication that it has a very low value.

Discussion.

The following mechanism of photosensitisation by chlorophyll explains all the principal features of the reaction between methyl red and phenylhydrazine or phenylhydrazine hydrochloride.

$$h\nu + \text{chl} \longrightarrow {}^{*}\text{chl}_{(a)}$$

$$^{*}\text{chl}_{(a)} \longrightarrow \text{chl} \quad \ldots \quad (1)$$

$$\text{chl}_{(a)} + \text{meR} \longrightarrow [\text{chl.meR}]_{(a)} \quad \ldots \quad (2)$$

$$[\text{chl.meR}]_{(a)} \longrightarrow \text{chl}_{(a)} + \text{meR} \quad \ldots \quad (3)$$

$$[\text{chl.meR}]_{(a)} + \text{Ph} \longrightarrow \text{chl} + \text{leuco meR} + \text{oxidised Ph} \quad \ldots \quad (4)$$

$$[\text{chl.meR}]_{(a)} + \text{PhHCl} \longrightarrow \text{chl} + \text{leuco meR} + \text{oxidised PhHCl} \quad (5)$$

On the basis of the commonly accepted principles, that for steady state, the rate of formation of an unstable intermediate product is equal to its rate of disappearance, we obtain for the velocity of formation of leuco methyl red, the following equation,

$$\frac{d\ [\text{meR}]}{dt} = \frac{h\nu\ .\ K_2\ [\text{meR}]}{K_1 + K_2\ [\text{meR}]} \times \frac{K_4[\text{Ph}]}{K_3 + K_4[\text{Ph}]}$$

* meR, Ph, $\text{chl}_{(a)}$, etc. are symbols for methyl red, phenylhydrazine and active chlorophyll, etc.

(1) If K_1 and K_3 are both small compared with K_2[meR] and K_4[Ph] respectively, *i.e.*, if the periods of the active chlorophyll molecule and of the intermediate complex of methyl red and active chlorophyll molecule are large, the equation becomes zero-molecular. Under such conditions obviously the quantum efficiency should be of the order of unity. This has been found to be the case with phenylhydrazine as reductant in green light both for methyl alcohol and benzene as solvents and for blue light only with methyl alcohol as solvent.

(2) If K_1 is large compared with K_2[meR] and K_3 also large compared with K_4[Ph], the reaction becomes unimolecular with respect to each of the reacting molecules of methyl red and phenylhydrazine. The quantum efficiency is necessarily very small. This is the case with phenylhydrazine as reductant with blue light in benzene solution.

(3) With phenylhydrazine hydrochloride as reductant, K_1 is always very large compared with K_2[meR] and hence the quantum efficiency is very low, and the velocity is unimolecular with respect to methyl red. The reaction could only be studied in methyl alcohol solution. In green light also K_3 is large compared with K_5[PhHCl], and the velocity is accordingly unimolecular with respect to phenylhydrazine hydrochloride. In blue light, however, K_3 and K_5Ph HCl are of the same order of magnitude, and therefore we found that the inverse of the unimolecular velocity constants plotted against the inverse oft he concentrations of phenylhydrazine hydrochloride is a straight line.

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A Lecture Experiment on Gas Diffusion.

By Arcot Viswanathan.

In order to demonstrate the change of pressure resulting from the different rates of diffusion of gases, the use of Cartesian divers has been found to be effective. Two coloured divers, so adjusted that one just sinks and the other just floats, are separated by a glass plate in a tall gas jar full of water. The rubber hung in the jar carries a tube strong enough to support the weight of a porous pot, which is held mouth upwards by the tube being bent twice at right angles over a short length. On placing a vessel of hydrogen over the pot, the top diver sinks. On removing it both rise. By bringing a vessel of carbon dioxide up under the pot the bottom diver rises.

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Received September 14, 1933.

REVIEW

A Manual of Practical Inorganic Chemistry. Qualitative Analysis and Inorganic Preparations,* by Dr. E. H. Riesenfeld. Translated by P. Rây. Published by Chuckervertty, Chatterjee & Co., Ltd. Calcutta, 1938, pp. 471+xxiii. 29 Figs. Price Rs. 6 (Indian), 9*s*. (Foreign).

There are no doubt numerous text-books on Analytical Chemistry but only in a few of them are attempts made at making the subject matter really useful and interesting to all, *viz.*, the beginner, the advanced student and the research worker. This book is an welcome addition to the literature in chemistry and is a masterly piece of work of the above nature. Both Riesenfeld and Rây are names well-known to workers in Analytical Chemistry and it is hoped that the present publication will be the constant companion of every young chemist who is receiving instruction through the medium of the English Language.

The most noteworthy feature of the book is the very successful attempt made at breaking away from the traditional pedagogic method of teaching analytical chemistry, first by the introduction, at suitable places, of very valuable, thorough and comprehensive directions for preparative chemistry with scrupulous and minute attention to purity, yield and economy. The preparations, which are described, have been judiciously selected and are typical, and although not too many yet appear on scrutiny to be quite sufficient for developing the manipulative skill of the operator to a very high order. Secondly, the introduction at requisite places of relevant chapters on theoretical chemistry, their discussion and presentation in a manner appealing to the intellect even of a beginner although incorporating matter of very recent growth, for the purpose of proper understanding and interpretation of analytical reactions, is a very remarkable achievement of which I find not much parallel in similar works of other authors in the English Language. Thirdly, the present volume, although a text-book on qualitative analysis, has a distinct quantitative bias and always aims at presenting the subject matter in such a way as to focus the attention of the worker on the quantitative side,

whereby he is expected constantly to be on the alert, and his imagination being thereby excited, qualitative analysis will ever appear to him to be interesting and never as a dull routine work. This aspect of the problem has further been supplemented by the incorporation, wherever possible, of those important reactions which are generally classed as "micro" and studied exclusively separately. The compilation of analytical tables is extremely clever and is another unique feature of the book, which I have not found elsewhere.

I would not presume to speak further about the text—as it will speak for itself—beyond stating that one would frequently find in it, methods, experimental technique, and explanations which are seldom found in books of similar nature.

A. M.

*Sir Prafulla Chandra Ray Seventieth Birthday Commemoration Volume, Journal of the Indian Chemical Society, Special Number.

Extracts from a few Press Opinions :

"**Nature**" * * * This volume of more than 800 pages contains 86 papers, and although the majority of these are naturally by Indians, chemists from Great Britain, America, Germany, Austria and Switzerland have also contributed. Pride of place is fittingly given to a paper by the President of the Chemical Society, Prof. G. T. Morgan, who gives an interesting account of recent high pressure work on the dehydrogenation of pyridine with anhydrous metallic chlorides. * * * The two other contributions from Great Britain are by Prof. M. W. Travers and Prof. F. G. Donnan, the former discussing the pyrolytic condensation and decomposition of ethane in the presence of hydrogen, whilst the latter presents a short but stimulating note on the thermodynamic functions of radiation. Students of the chemistry of polysaccharides will welcome a valuable resumè of recent investigations in this field from the pen of Prof. H. Pringsheim. Another paper of great interest by Prof. Franz Fischer summarises the valuable work on the utilisation of coal gas. * * * Prof. M. N. Saha has, however, written a remarkably able review entitled "Spectroscopy in the Service of the Chemist." The contributions to this commemoration volume reach a high standard and augur well for the future of the schools of Chemistry in India of which Sir Prafulla may with justice regard himself as the Founder.

"**Journal of the Franklin Institute**" The reviewer believes it will be sometime before he again sees a special number of a chemical society journal similar to this. The Indian Chemical Society may well be proud of its Commemoration Volume dedicated to a world-renowned pioneer of chemical research in India, Sir Prafulla Chandra Ray * * * It is very, very seldom that such a collection of authors will be found between the covers of a chemical journal * * * After reading the list of authors all chemists will have prepared themselves for a series of papers touching upon almost every phase of chemical science and dealing with the subjects in a clear, concise and authoritative manner. In all, there are 86 papers of which only brief mention can be made here. Colloid chemistry has always received considerable attention from Indian chemists and is well represented. * * *

"**Current Science**" * * * I have nothing but praise for the wealth of diverse and interesting material here presented. From the first item, appropriately introduced by the President of the Chemical Society, London, throughout until the last, by Dr. Franz Fischer of the Kaiser-Wilhelm Institut für Kohlenforschung, Mulheim-Ruhr, every contribution justifies its inclusion, and the prodigality of subjects recalls the bill-of-fare with which pre-war transatlantic liners were wont to dazzle their less fastidious passengers. A rough analysis of the 86 memoirs apportions their subjects among the following branches :—Physical (8), organic (7), colloidal (5), pyro-chemical and biochemical (each 4), molecular (3), photochemical (2), thermodynamic, therapeutic and microchemical (each 1). * * * Thus the promoters of the volume, and the collaborators who gallantly responded to their invitation deserve warm congratulation on the success of their enterprise. * * *

Reduction of Chloral Hydrate and Chloral Acylchlorides.

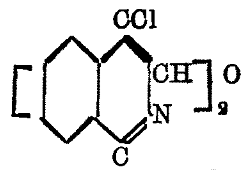
By Gajanan Waman Deodhar.

Chloral hydrate has been reduced with aluminium amalgam giving a product (b. p. 96-98°), which consists mainly of dichloraldehyde hydrate as it gives dichloroethylidene diacetate, $CHCl_2\cdot CH(OCOCH_3)_2$ (Delacre, *Bull. Soc. Chim.*, 1930, **48**, 715) with acetic anhydride and sulphuric acid and dichloroacetal with alcohol and sulphuric acid and dichloraldehyde by distillation with sulphuric acid. Dichloraldehyde is further confirmed by the preparation from it of $\alpha\beta\beta$-trichloroethyl acetate, $CHCl_2\,CHCl\cdot OCOCH_3$ (Delacre, *loc. cit.*) by the action of acetyl chloride and of glyoxime by the action of hydroxylamine.

Chloral acetylchloride, $CCl_3\cdot CHCl\cdot OCOCH_3$, was reduced by Curie and Milliet (*Compt. rend.*, 1901, **133**, 745; *Ber.*, 1876, **9**, 1611) by means of zinc and acetic acid. They described the reduction product as $\alpha\beta$-dichloroethyl acetate, $CH_2Cl\cdot CHCl\cdot OCOCH_3$ (*cf.* Natterer, *Monatsch.*, 1882, **3**, 459), who prepared it by the action of acetyl chloride on chloraldehyde hydrate. This seemed to be unlikely and hence a study of the reduction product was taken up. The same product is obtained by reducing chloral diacetate, $CCl_3\cdot CH(OCOCH_3)_2$ with zinc and acetic acid. This shows that the presence of a Cl atom in the α-position in the reduction product is unlikely. The reduction product absorbs two atoms of bromine. It behaves like dichloraldehyde towards phenylhydrazine, semicarbazide, etc., and gives dichloraldehyde hydrate on treatment with concentrated ammonia solution. All these properties show that the reduction product is β-dichlorovinylacetate, $CCl_2 : CH\cdot OCOCH_3$. This can hydrolyse to form dichlorovinyl alcohol which would give rise to dichloraldehyde.

β-Dichlorovinyl acetate gives with dry ammonia β-dichlorovinylamine. The latter gives with benzoyl chloride and caustic soda a

substance m.p. 199° (decomp.) to which the following constitution is provisionally given



Other β-dichlorovinyl esters were prepared by reduction of the condensation products of chloral with acyl chlorides with zinc and acetic acid.

EXPERIMENTAL.

Preparation of chloral acylchlorides.—The acid (1 mol.) was heated with thionyl chloride (2 mols.) on a water-bath with a reflux condenser till the evolution of SO_2 and HCl slackened. The mixture was then cooled and chloral (a little more than 1 mol.) was added. The mixture was then shaken with a few drops of concentrated sulphuric acid when the condensation took place with the evolution of heat. The condensation is less vigorous the higher the molecular weight of the acid and in some cases it is necessary to start the reaction by heating the mixture. The condensation products are liquids and some of them decompose on distilling under reduced pressure. In such cases the substance was washed, dried and reduced with zinc and acetic acid.

Reduction of chloral hydrate.—Chloral hydrate (84 g.) was dissolved in water (100 c.c.) and reduced with aluminium amalgam prepared from aluminium foil (13·5 g.) and added in three lots. The mixture was extracted several times with ether and a liquid (66 g. b. p. 96-98°) was obtained on removing the ether. This gave dichloraldehyde with partial decomposition on distillation with sulphuric acid.

γ-Dichlorocrotonic acid.—Dichloraldehyde (18 g.) was mixed with malonic acid (12 g.) and pyridine (15 g.). The reaction which immediately started with evolution of CO_2 was completed by heating on the water-bath. The mixture was heated with dilute sulphuric acid and extracted with ether. A sticky liquid which was obtained on the removal of ether gave a crystalline solid (2·5 g.) on the addition of a little water. The solid forms white feathery plates from water, m.p. 100-01°. (Found: Cl, 45·72; Eq. wt. 158·8. $C_4H_4O_2Cl_2$

requires Cl, 45·75 per cent; Eq. wt., 154·9). The mother liquor from above gave a sticky residue which solidified on keeping in a desiccator. This was purified from chloroform and gave short prisms, m.p. 117-18°. It was found to be an acid containing chlorine and of Eq. wt., 208·9.

β-Dichlorovinyl acetate.—Chloral acetylchloride (100 g.) (Meyer and Dulk, *Annalen*, 1874, **171**, 67), prepared by treating water-free chloral with an equivalent quantity of acetyl chloride in the presence of sulphuric acid, was reduced by shaking in a bottle with acetic acid (150 c.c.) and zinc dust (60 g.) which was added in small quantities at a time. After the reduction was complete, the mixture was filtered to remove zinc acetate and unchanged zinc and the filtrate diluted with water. The heavy oily liquid (60 g.) separating was dried over sulphuric acid and distilled at 148-49°. (Found: Cl, 45·8, M. W. 154·5. $C_4H_4O_2Cl_2$ requires Cl, 45·8 per cent; M. W., 154·9). Curie and Milliet (*loc. cit.*) recorded the b.p. as 146°. The same product is obtained by the reduction of chloral diacetate (Meyer and Dulk, *loc. cit.*) with zinc and acetic acid in a similar way.

β-Dichloro-αβ-dibromoethyl acetate was obtained as a liquid by treating β-dichlorovinyl acetate with bromine, b.p. 127°/40 mm. (Found: Br, 50·72. $C_4H_4O_2Cl_2Br_2$ requires Br, 50·72 per cent). The product decomposes on keeping.

β-Dichlorovinylamine.—β-Dichlorovinyl acetate (80 g.) was mixed with chloroform (50 c.c.) and a few g. of powdered anhydrous sodium sulphate and a brisk current of dry ammonia was passed through the mixture which was cooled with water. After 2 hours when the smell of the ester disappeared, the mixture was washed with water and dried over caustic soda and the chloroform was evaporated off. The sticky residue on dissolving in alcohol and keeping gave a white solid (2·5 g.), which crystallised in needles from alcohol, m.p. 109°. (Found: N, 12·0; Cl, 63·4. $C_2H_3NCl_2$ requires N, 12·5; Cl, 63·4 per cent).

It gave with benzoyl chloride in presence of caustic soda a solid which crystallised in needles, m.p. 199° (decomp.) from alcohol. (Found: N, 8·8; Cl, 20·8. $C_{18}H_{10}ON_2Cl_2$ requires N, 8·6; Cl, 20·8 per cent).

Action of aqueous ammonia.—β-Dichlorovinyl acetate (72 g.) was dissolved in concentrated aqueous ammonia while cooling in ice. The solution was quickly acidified with dilute sulphuric acid and extracted with ether. The liquid (40 g.) that remained after removal

of ether was identified with the reduction product of chloral hydrate.

β-Dichlorovinyl acetate gave with malonic acid in presence of pyridine γ-dichlorocrotonic acid, with phenylhydrazine glyoxal-osazone, m. p. 179° (Found: N, 23·5. $C_{14}H_{14}N_4$ requires N, 23·5 per cent) and with semicarbazide hydrochloride disemicarbazone of glyoxal. (Found: N, 49·3. $C_4H_8O_2N_6$ requires N, 48·9 per cent).

Chloralpropionyl chloride, b. p. 120°/40 mm. (Found: Cl, 59·4. $C_5H_6O_2Cl_4$ requires Cl, 59·1 per cent).

β-Dichlorovinyl propionate, b. p. 90-92°. (Found: Cl, 42·0. $C_5H_6O_2Cl_2$ requires Cl, 42·0 per cent).

β-Dichloro-αβ-dibromoethyl propionate, b. p. 145-46°/39 mm. (Found: Br, 48·3. $C_5H_6O_2Cl_2Br_2$ requires Br, 48·6 per cent).

Chloral-n-butyryl chloride, b. p. 128°/36 mm. (Found: Cl, 55·6. $C_6H_8O_2Cl_4$ requires Cl, 55·9 per cent).

β-Dichlorovinyl n-*butyrate*, b. p. 100-101°/36 mm. (Found: Cl, 39·1. $C_6H_8O_2Cl_2$ requires Cl, 38·7 per cent).

β-Dichloro-αβ-dibromoethyl n-*butyrate*, b. p. 162-64°/40 mm. (Found: Br. 46·5. $C_6H_8O_2Cl_2Br_2$ requires Br, 46·3 per cent).

β-Dichlorovinyl benzoate was obtained as needles, m. p. 34-35°. (Found: Cl, 32·6. $C_9H_6O_2Cl_2$ requires Cl, 32·7 per cent).

β-Dichlorovinyl cinnamate was obtained as needles, m. p. 70°. (Found: Cl, 29·2. $C_{11}H_8O_2Cl_2$ requires Cl, 29·3 per cent).

β-Dichloro-αβ-dibromoethyl dibromocinnamate was obtained as needles, m. p. 87-88° (Found: Br, 57·0. $C_{11}H_8O_2Cl_2Br_4$ requires Br, 56·8 per cent).

The author is thankful to the University of Bombay for the grant of Springer Research Scholarship and to Dr. A. N. Meldrum for his interest in the work.

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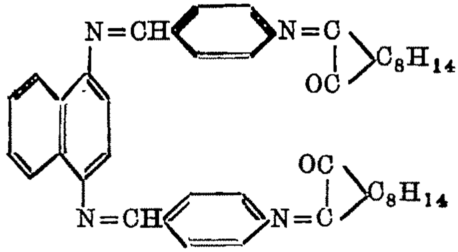
Received May 1, 1933.

Bisiminocamphor Derivatives with Exalted Optical Activity.

By S. M. Patel and P. C. Guha.

Forster and Thornley (*J. Chem. Soc.*, 1909, **95**, 942) observed that bisiminocamphor derivatives display remarkably high rotatory power, and this was later ascribed to an optimum association of azethenoid groups, conjugated linkages and a benzene ring within a narrow molecular compass (Forster and Spinner, *ibid.*, 1919, **115**, 889). B. K. Singh and his collaborators also have prepared numerous bis-iminocamphor derivatives (*ibid.*, 1919, **115**, 566; 1920, **117**, 1699; 1921, **119**, 1971 ; *J. Indian Chem. Soc.*, 1926, **3**, 385; 1929, **6**, 107; 1930, **7**, 545, 771; 1931, **8**, 95, 181, 345, 623; 1932, **9**, 1) including 1:4-naphthylenebisiminocamphor and *pp′*-bisiminocamphordipheny-lamine, with molecular rotation 13416° (pyridine) and 14231° (ethyl alcohol) respectively. These two compounds, within a narrow mole-cular compass, embrace two azethenoid groups and included in their naphthalene or benzene rings conjugated double linkages aggre-gating nine and ten respectively, thus confirming the above-quoted generalisation.

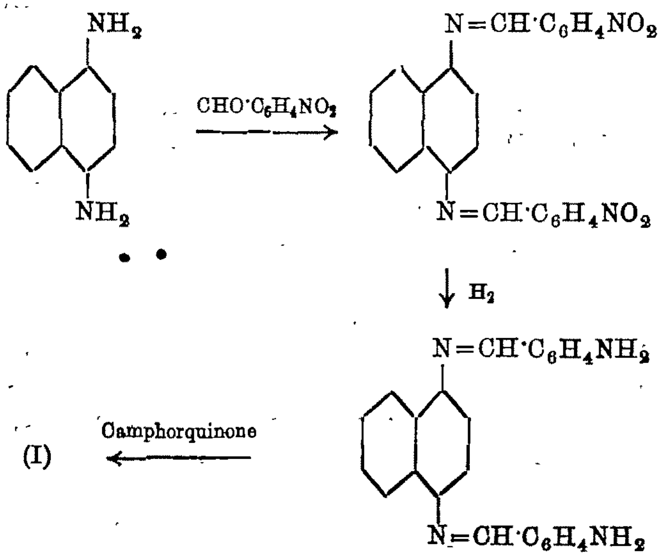
Maintaining the foregoing typical molecular arrangement, we have now prepared 1:4-naphthylenebisiminobenzylideneiminocamphor in



(I)

which the number of conjugated double linkages has been increased to 17; correspondingly, the molecular rotation reaches 22050° in pyridine for the mercury yellow line 5780. This observation was made in collaboration with Mr. S. M. Mistry and communicated to the Indian Science Congress, 1931.

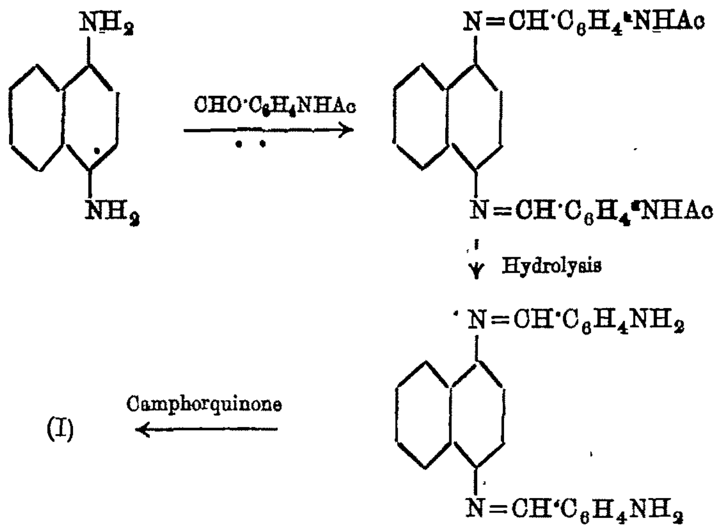
The preparation of this compound followed some unsuccessful attempts. An obvious method would be to condense with 1:4-naphthylenediamine two molecules of the condensation product of *p*-aminobenzaldehyde with camphorquinone, but the latter could not be obtained owing to the readiness with which the aldehyde undergoes polymerisation (*cf.* Gabriel, *Ber.*, 1883, 16, 2000). The next attempt was to proceed through *p*-nitrobenzaldehyde according to the following scheme:



The acid reduction of bisnitrobenzylidenenaphthylenediamine could not be effected, the azomethine group being very sensitive to mineral acids, while reduction with alcoholic ammonium sulphide, zinc dust and acetic acid or ferrous sulphate and ammonia yielded only tarry products.

Finally, we condensed *p*-acetaminobenzaldehyde with 1:4-naphthyenediamine, removed the acetyl groups by dilute hydrochloric acid in

alcohol, and condensed the resulting bisaminobenzylidenenaphthylenediamine with camphorquinone as follows:



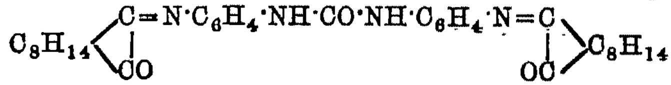
(I)

It is well known that the carbonyl group exalts optical rotation in organic compounds (*cf.* Hilditch, *J. Chem. Soc.*, 1911, **99**, 224) and it seemed of interest to ascertain the effect on rotation produced by interrupting a conjugated system with a carbonyl or a carbamido group. The introduction of a carbonyl, carbamido or an oxamido group between two benzene rings in *pp*-diphenylenebisiminocamphor from benzidine and camphorquinone, and a comparison of the resulting rotations with those of the corresponding compounds of benzidine and diaminodiphenylmethane would indicate the effect of such groups combined with interruption of conjugation.

While *pp'*-diaminobenzophenone* could not be condensed with camphorquinone, the bisiminocamphor derivative of *pp*-diaminodiphenylcarbamide and *pp*-diaminodiphenyloxamide show the following rotations, the values comparing very favourably with that of the benzidine compound; it is thus clear that the decrease caused by breaking the continuity of conjugated double bonds is more than compensated by the introduction of the carbamido and the oxamido groups.

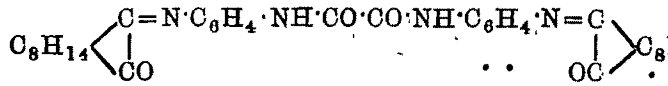
* For dissimilar behaviour of diaminodiphenylmethane and diaminobenzophenone compare Guha and Mistry (*J. Indian Inst. Sci.*, 1932, **15A**, 27).

M_D in $CHCl_3$.



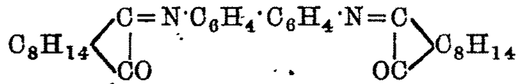
8911°

(II)



12094°

(III)

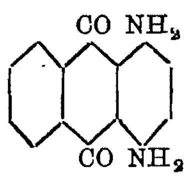


5565°

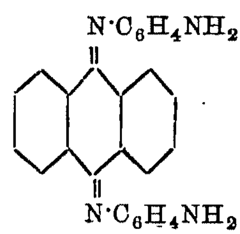
Resembling *pp*-diaminobenzophenone, *pp*-diaminoazobenzene (*i*), *pp*-diaminodiphenylazodicarbonamide (*ii*), 1:4-diaminoanthraquinone (*iii*), and bisaminophenylanthraquinonedimide (*iv*), could not be made to react with camphorquinone; the compounds sought, particularly that from the last named, were expected to show very high rotatory power.*

(*i*) $NH_2C_6H_4{\cdot}N{=}N{\cdot}C_6H_4NH_2$ (*ii*) $N{\cdot}CO{\cdot}NH{\cdot}C_6H_4NH_2$ $\parallel$ $N{\cdot}CO{\cdot}NH{\cdot}C_6H_4NH_2$

(*iii*)



(*iv*)



EXPERIMENTAL.

Condensation of p-*nitrobenzaldehyde with* 1:4-*naphthylenediamine*.—The naphthylenediamine was prepared by coupling diazotised aniline with α-naphthylamine and reducing the product with zinc and boiling water (*Ber*., 1889, 22, 1381). To naphthylenediamine hydrochloride (2·4 g.) dissolved in a little water, crystalline sodium acetate was added in excess. *p*-Nitrobenzaldehyde (3·5 g.) in 95% alcohol

* These experiments were conducted in collaboration with Mr. S. M. Mistry and a preliminary report published in the Proc. Indian Science Cong., 1932, p. 220.

was then added and the mixture heated under reflux for 8 hours when gradually the dinitro-compound separated as a reddish-yellow precipitate which was washed with hot alcohol and recrystallised from glacial acetic acid, m.p. 281°. (Found: N, 13·04. $C_{24}H_{16}O_4N_4$ requires N, 13·2 per cent).

Attempts to reduce the dinitro compound.—Reducing agents involving the use of mineral acids could not be used because they attacked azomethine group. Reduction was successively tried wit alcoholic ammonium sulphide, sodium sulphide and water, zinc dust and glacial acetic acid and lastly with ferrous sulphate and ammonia. The ethereal extract of the free diamine exhibited in all cases a green fluorescence and on evaporation of ether left only a tarry semi-solid mass.

Condensation of p-*acetaminobenzaldehyde with* 1:4-*naphthylenediamine.*—The yellow crystalline acetamino compound was obtained by boiling *p*-aminobenzaldehyde hydrochloride with acetic anhydride and fused sodium acetate (*Monatsh.*, 1903, **24**, 88), m.p. 154-55° (not 161° as given in the literature).

A solution of naphthylenediamine hydrochloride (2·3 g.) in water, excess of sodium acetate and acetaminobenzaldehyde (3·5 g.) in 95% alcohol was heated under reflux for 2 hours. The precipitated greenish powder crystallised from pyridine in brown needles, m.p. 317°. (Found: N, 12·6. $C_{28}H_{24}O_2N_4$ requires N, 12·5 per cent).

Hydrolysis of the acetyl compound.—Hydrolysis could not be effected by boiling with *N*/2, 2*N*, and 5*N* alcoholic potash, while stronger alkali gave tarry products. The diacetyl compound was next mixed with a small quantity of alcohol and treated with dilute hydrochloric acid, forming a clear solution on being gently warmed; this was cooled in ice and treated with ice-cold concentrated hydrochloric acid when the *hydrochloride* of bis-*pp*-aminobenzylidenaphthylenediamine was obtained as a yellowish-red crystalline product. (Found: N, 13·12. $C_{24}H_{22}N_4Cl_2$ requres N, 12·81 per cent).

1:4-*Naphthylenebisiminobenzylideneiminocamphor* (I).—The hydrochloride of bis-*pp*-aminobenzylidene-1:4-naphthylenediamine (4·3 g.) mixed with water and excess of sodium acetate was treated with camphorquinone (3·5 g.) in 95% alcohol and boiled for 2 hours. On cooling, deep-red crystals were deposited which after being washed with water and petrol crystallised from absolute alcohol, m.p. 239°. (Found: N, 8·6 $C_{44}H_{44}O_2N_4$ requires N, 8 4 per cent). The rotation observed for 0·1100 g. of the substance

dissolved in 250 c.c. of dry pyridine in a 1 dcm. tube was α_{5780} = 1·47°; whence $[\alpha]^{25°}_{5780}$ = 3340·9°, corresponding to $[M]^{25°}_{5780}$ = 22050°.

An improved method of preparing pp′-*diaminodiphenylcarbamide*.—The method of Schiff and Ostrogovitsch (*Annalen*, 1896, **293**, 376) gave a very poor yield most of which was, however, insoluble in boiling concentrated hydrochloric acid. The condensation of acet-*p*-phenylenediamine with urea proceeded quite smoothly according to the method of Guha and Mistry (*J. Indian Chem. Soc.*, 1930, **8**, 793) in boiling amyl alcohol, evolution of ammonia terminating after 7 hours. The pure colourless diacetyl compound melted at 343°.

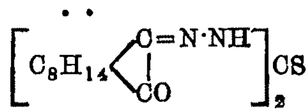
Hydrolysis could not be effected by boiling for a long time with dilute hydrochloric acid, but the powdered acetyl compound dissolved in gently boiling concentrated hydrochloric acid for ½ hour. The filtered solution on concentration gave a white crystalline hydrochloride.

Diaminodiphenylcarbamide and camphorquinone: Formation of carbamidodiphenylenebisiminocamphor (II).—A mixture of diaminodiphenylcarbamide hydrochloride (1·6 g.), excess of sodium acetate and camphorquinone (3·5 g.) in 95% alcohol was boiled under reflux for 2 hours when the solution became deep red. The greenish yellow precipitate obtained on adding water was washed with petrol to remove camphorquinone and yielded on careful crystallisation from alcohol two isomeric compounds (A and B). The substance (A) was nearly insoluble in alcohol and was obtained as a greenish precipitate after several crystallisation from 98% alcohol, m.p. 280°. Compound (B) was obtained as an orange powder after crystallisation from 70% alcohol, m.p. 266°. (Found: (A) N, 10·2; (B) N, 10·4. $C_{33}H_{38}O_3N_4$ requires N, 10·4 per cent). 0·2110 G. of the substance (A), dissolved in 25 c.c. of chloroform gave in 0·5 dcm. tube α_D 6·99°, corresponding to $[M]_D$=8911·4°. On account of the sparing solubility of (B) in solvents its molecular rotation could not be determined.

Oxamidodiphenylenebisiminocamphor (III).—The yellow crystalline compound obtained from the hydrochloride of diaminodiphenyloxamide (3·42 g.), prepared according to Mistry and Guha (*loc. cit.*), excess of sodium acetate and camphorquinone (3·5 g.) by boiling in 95% alcohol crystallised from alcohol in yellow shining leaflets, m.p.

183°. (Found: N, 9·6. $C_{34}H_{38}O_4N_4$ requires N, 9·8 per cent). 0·103 G. of the substance in 25 c.c. chloroform in a 0·5 dcm. tube gave $\alpha_D = +3{\cdot}4°$, whence $[\alpha]_D^{25} = 1650{\cdot}4°$ and $[M]_D = 9341{\cdot}7°$. 0·078 G. of the substance in 100 c.c. pyridine gave (0·5 dcm. tube) $\alpha_D = 0{\cdot}78°$, whence $[\alpha]_D^{25} = 2186{\cdot}9°$ and $[M]_D = +12095$.

Thiocarbobishydrazinocamphor.



Thiocarbohydrazide (1 mol.) and camphorquinone (2 mols.) were heated for 30 hours in absolute alcohol using anhydrous sodium sulphate as condensing agent. The yellow plates separating out on cooling, were washed successively with water and petrol and recrystallised from alcohol in yellowish-brown shining plates, m.p. 226°. (Found: S, 8·2. $C_{21}H_{30}O_2N_4S$ requires S, 7·9 per cent). 0·94 G. of the substance dissolved in 100 c.c. chloroform gave in a 0·5 dcm. tube $\alpha_D = +1{\cdot}82°$, whence $[M]_D = +1557°$.

Condensation of 2:2′-diaminodiphenyl and 1:2-naphthylenediamine with camphorquinone could not be effected by the above methods.

The authors' thanks are due to Sir Martin Forster, F.R.S. for the kind interest he has taken in this investigation.

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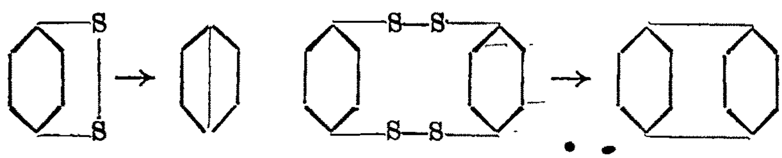
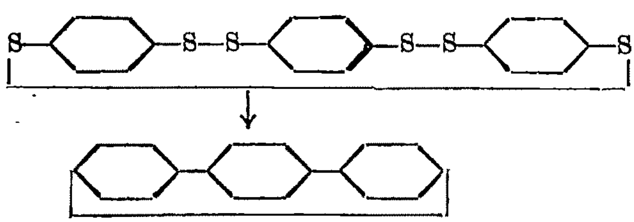
Synthesis of *pp'*-Diphenylenedimonosulphide.

By V. C. Parekh and P. C. Guha.

p-Phenylenedimercaptan gives on oxidation a white amorphous powder possessing the empirical formula $(C_6H_4S_2)_n$. As the disulphide (or polysulphide?) so formed is insoluble in all organic solvents it has not been possible yet to solve by determining its molecular weight the question as to what is the nature of complexity of the molecule. It was thought worth while to try the action of some suitable desulphurising agents upon the di-(or poly?) sulphide with the hope that the desulphurised product would be an aromatic hydrocarbon (I), (II) or (III) and which in all probability would be soluble in organic solvents and would lend itself to molecular weight determination.



(I) (II)



(III)

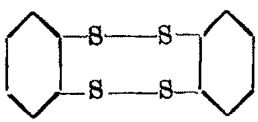
In order to remove the sulphur atoms, desulphurising agents such as sodium, molecular sodium, mercury, mercuric chloride and nitrate, *natur cupfer* and freshly reduced copper have been tried under varying conditions of experiments. Of all these reagents *natur cupfer* and freshly reduced copper have only been found to be suitable for the purpose and the product isolated from the reaction

mixture melted after purification at 148°. The analytical results and the molecular weight (216) show that the compound possesses the formula ($C_{12}H_8S_2$) and is evidently a product of partial desulphurisation of the original polysulphide.

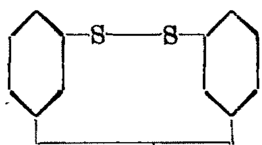
Now there are two possible structures (V) and (VI) which can be attributed to this compound, the former arising from *pp*-diphenylenedisulphide (IV) (or from a polysulphide like

$$S_2\left\langle\begin{matrix} C_6H_4—S_2—C_6H_4 \\ C_6H_4—S_2—C_6H_4 \end{matrix}\right\rangle S_2$$

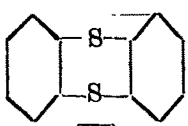
by the loss of two sulphur atoms from one side and the latter by the elimination of one atom of sulphur from each of the disulphide groupings.



(IV)



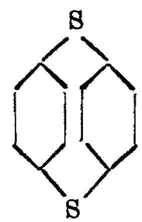
(V)



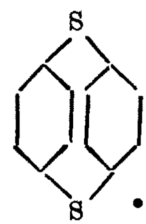
(VI)

The formula (V) has been rejected on the ground that our compound does not give any trace of mercaptan when subjected to the action of reducing agents; moreover, the removal of both of the sulphur atoms from one of the molecules leaving the other half intact, does not seem to be very likely. As the yield of the compound is very poor (*vide* experimental) it has not been possible to adduce any further experimental proof in confirmation of the symmetrical dimonosulphide structure. It will be seen that although the original object *viz.*, the conversion of the tetrasulphide into *pp′*-diphenylene has not been fully realised, this reaction has, however, been employed with advantage to solve the molecular complexity of the original polysulphide which can now be regarded as *pp′*-diphenylenetetrasulphide and that it has yielded a hitherto unknown type of compound in which the two pairs of *para* carbon atoms are linked through sulphur. The question now naturally arises as to whether the synthesis of this *pp′*-diphenylenedimonosulphide suports or contradicts Kaufler's folded structure of diphenyl

(*Annalen*, 1907, **351**, 151) which according to recent work (*J. Amer. Chem. Soc.*, *Chemical Reviews*, 1933, **12**, 269) has been definitely proved to be wrong. The fact that diphenyl has been proved to possess an extended co-planar structure and that attempts to convert its *pp'*-diiodo derivative into *pp'*-diphenylene have resulted in faliure (Sircar and De, *J. Indian Chem. Soc*, 1926, **3**, 245) do not necessarily mean that a substance like diphenylenedimonosulphide should be incapable of existence. In diphenyl two nuclear carbon atoms are directly connected and in the other the two pairs of *para* carbon atoms are connected through sulphur, which must exert some sort of effect on the valency directions in consequence of which the two pair of *para*-carbon atoms might come sufficiently near to be linked through sulphur. The phenylene residues in compound $C_{12}H_8S_2$ can be in one plane as shown in A or in a plane perpendicular or inclined at some angle to that of the paper as shown in B. Substitution products of this



(A)



(B)

interesting compound might lend themselves to optical resolution due to the asymmetry of the molecule as a whole. Model B even with one substituent will make the molecule asymmetric; whereas there is the possibility of substituents making model A assume an asymmetric structure due to restricted rotation on the basis of which the optical activity of the diphenyl derivatives is now explained (*Chem. Ind.*, 1926, **45**, 831, 864, 884). The effect of other groups like $(CH_2)_n$, CO and $(NH)_n$ in bridge formation between two pairs of *para* carbon atoms of two benzene molecules is under investigation.

Experimental.

p-*Phenylenedisulphochloride* was prepared starting from sulphanilic acid *via* potassium xanthosulphonate of benzene ($KO_3S\text{-}C_6H_4\cdot S\cdot CS\cdot OEt$) and potassium benzene disulphonate. The disul-

phochloride melted at 139° and not at 131° as given by Koerner and Monslise (*Gazzetta*, 1876, **6**, 140), Jackson and Wing (*Am. Chem. J.*, 1887, **9**, 332) give 139°, Zincke and Frohneberg (*Ber.*, 1909, **42**, 2721) give 138°.

p-*Phenylenedimercaptan.*—(*a*) The method of Sestini (*Ber.*, 1876, **9**, 584) for reduction of the sulphochloride by means of tin and hydrochloric acid was found not to give more than 20 % of theoretical yield.

(*b*) Reduction of the sulphochloride (1 mol.) by means of hydrochloric acid (18 mols.) and zinc dust (6·5 mols.) added portion-wise under reflux did not give more than 25 % yield.

(*c*) The method given in "Organic Synthesis", Vol. I, p. 71 (for the preparation of thiophenol) was also tried with the result that the yield could only be raised up to 30 % of theory.

(*d*) *The best method.*—An intimate mixture of the disulphochloride (31 g.) and zinc dust (100 g.) was suspended in water (150 c. c.) in a three-necked round bottomed flask (1 litre capacity) fitted with a long upright condenser. Concentrated hydrochloric acid (300 c.c.) was then added drop by drop during half an hour from a separating funnel while the mixture was stirred by a mercury-sealed stirrer. (It was found that the commercial hydrochloric acid gave a better yield than when Merck's pure hydrochloric acid was used.) The stirring was continued for half an hour after addition of the acid was over. The flask was then heated gently for about an hour and then vigorously with the addition of some more zinc (20 g.) and hydrochloric acid (100 c.c.); rapidly cooled in ice-water and the contents filtered. The white precipitate was digested with absolute alcohol thrice and the small quantity of insoluble residue was again treated with zinc dust (20 g.), hydrochloric acid (100 c.c.) and water, boiled, cooled as before and extracted with absolute alcohol. The concentrated alcoholic extracts on being poured into an excess of water gave the mercaptan as a white precipitate. It crystallised from 95 % alcohol, m. p. 96-97° which rose to 98° on recrystallisation; yield, 12 g. (75 % of theory).

Oxidation of the dimercaptan has been effected by Lustig (*J. pr. Chem.*, 1890, *ii*, **41**, 206) and also by Frohnsberg (*Ber.*, 1909, **42**, 2727) by various oxidising agents. We found it more convenient, however, to adopt the following method:

Ferric chloride (120 g.) dissolved in hot alcohol (150 c.c.) was added to the mercaptan (15 g.) dissolved in the minimum quantity of hot alcohol when a yellowish precipitate was formed. The reaction mixture was heated for about two minutes more, filtered hot, washed several times with hot alcohol under suction and dried in a vacuum desiccator. It is an amorphous powder insoluble in organic solvents and not melting even at 300°. (Found: S, 45·93. $(C_6H_4S_2)_n$ requires S, 45·71 per cent)..

Desulphurisation with reduced copper in a current of carbon dioxide.—A narrow hard glass tube (18″ long), sealed at one end, was charged with powdered magnesite (2″) followed by an intimate mixture of the polysulphide (4 g.) and freshly reduced copper (10 g.) and then a column of reduced copper (2″) with asbestos plugs separating them. The open end of the tube was bent at an angle of about 120° drawn narrower and immersed under water contained in a beaker. The burner below magnesite was first ignited and a slow current of carbon dioxide allowed to bubble through water, the burners below the copper powder and the substance were lighted gradually and the heating continued for 3 hours when a few drops of an oil collected on the surface of water. The ethereal extract of the oil was dried with anhydrous magnesium sulphate and yielded after distilling off the ether a thick oily substance which contained sulphur. The ether and benzene extracts of the contents of the tube gave only a very small quantity of tarry mass which could not be purified. The metallic residue evolved hydrogen sulphide profusely on treatment with hydrochloric acid.

A modified process.— An intimate mixture of the polysulphide (7·5 g.) and reduced copper (15 g.) was heated in a round-bottomed flask fitted with a vertical tube at its mouth and carrying a calcium chloride guard tube at the end for 2,6 and 12 hours at 200°, 250° and 300° in a metal bath, making altogether nine experiments. It was only in the last experiment that some reaction was found to take place. The extracts of the contents of the flask in hot dry benzene yielded a small quantity of a brownish-yellow heavy oil. From six such experiments only 0·9 g. of the thick oil could be collected. Attempts at its purification failed due to its extreme solubility in all organic solvents. Some crystals, however, separated from the oil on standing in a vacuum desiccator for about two months which were carefully separated by filtration under suction and then washed with dry benzene, m. p. 146-47°; after crystallisation from benzene

the m. p. rose to 148°, on recrystallisation the m.p. remained unchanged. The substance was recovered unchanged after being boiled with zinc and hydrochloric acid and did not contain any mercaptan. [Found: (micro* method) C, 67·94; H, 3·99; S, 28·84, M. W., 216. $C_{12}H_8S_2$ requires C, 66·66; H, 3·7; S, 29·62 per cent. M. W., 216).

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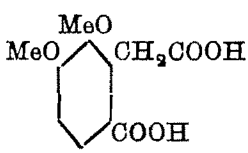
* 0·024 G. of the substance was sent to Prof. Pregl of the University of Graz in December 1930 for micro analysis and molecular weight determinations and these results have been communicated to us by Dr. August Verdino, the lamentable death of Prof. Pregl having occurred in the meantime.

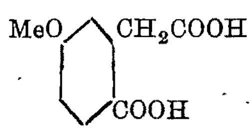
Synthesis of 5 : 6-Dimethoxyhomophthalic Acid and of some Monomethoxy-homophthalic Acids.

By Satyendra Nath Chakravarti and M. Swaminathan.

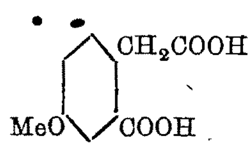
During the course of our synthetical experiments on ψ-opianic acid and berberine alkaloids we required some hydrindones and homophthalic acids as the starting substances. Careful study of the literature revealed the fact that a majority of the monomethoxy-homophthalic acids and 5 : 6-dimethoxyhomophthalic acid are still unknown. In this paper the synthesis of 5 : 6-dimethoxyhomophthalic acid (I) and 4- and 5-methoxyhomophthalic acids (III, II) is recorded. The synthesis of 3-and 6-methoxyhomophthalic acids is reserved for a future communication.



(I)



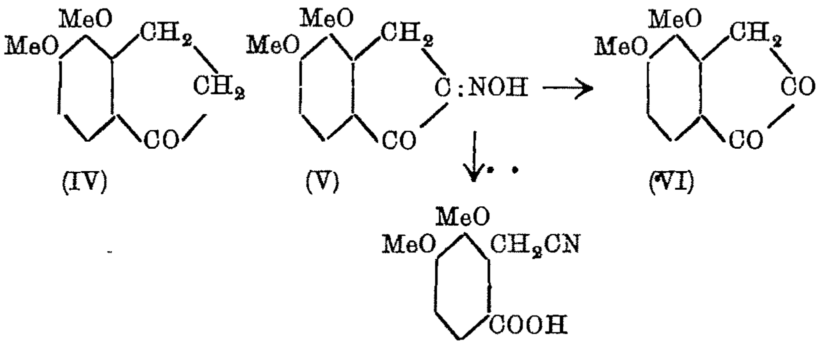
(II)



(III)

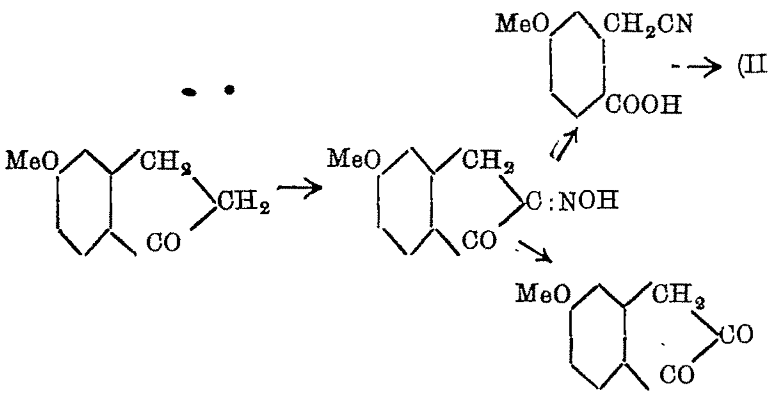
5 : 6-Dimethoxyhomophthalic acid was synthesised in the following manner: *o*-Veratraldehyde was first converted into 2 : 3-dimethoxycinnamic acid according to the conditions described before (Chakravarti, *J. Indian Chem. Soc.*, 1929, **6**, 223). The cinnamic acid was then reduced and converted according to the method of Ruheman (*Ber.*, 1920, **53**, 275) into 4 : 5-dimethoxyhydrindone (IV), the *iso*nitroso derivative of which was converted into 2-carboxy-5 : 6-dimethoxyphenylacetonitrile (VII) in a yield of about 95% by the action of toluene-*p*-sulphonyl chloride. The cyanide was hydrolysed to 5 : 6-dimethoxyhomophthalic acid in an yield of about 90%. This acid was also obtained in a poorer yield by the direct oxidation of 4 : 5-dimethoxyhydrindone (IV) with dichromate and sulphuric

acid. During the course of these experiments 4:5-dimethoxy-1:2-diketohydrindene (VI), m.p. 150°, was also isolated.



(IV) (V) (VI) (VII)

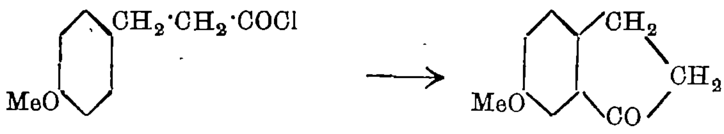
5-Methoxyhomophthalic acid (II) which had previously been obtained by Ingold and Pigott (*J. Chem. Soc.*, 1923, **123**, 1503) has now been prepared in a better yield by the application of the above method. 5-Methoxy-1:2-diketohydrindene (VIII), m.p. 152° was also isolated.



(VIII)

4-Methoxyhomophthalic acid was also prepared by a method similar to that outlined above. 6-Methoxyhydrindone (X) was first prepared by Ingold and Pigott (*loc. cit.*) starting from 6-nitrohydrindone. Perkin and Robinson (*J. Chem. Soc.*, 1907, **91**, 1081) were unable to isolate this hydrindone by the action of aluminium chloride upon *p*-methoxyhydrocinnamoyl chloride (IX). We have now succeeded in converting the acid chloride directly into 6-methoxy-

hydrindone by the action of aluminium chloride in nitrobenzene solution in an yield of about 20%.



(IX) (X)

6-Methoxyhydrindone (X) was then converted into the *iso*nitroso compound and the latter into 4-methoxy-2-carboxyphenylacetonitrile which was smoothly hydrolysed to 4-methoxyhomophthalic acid (III).

Experimental.

4:5-Dimethoxyhydrindone was prepared according to the directions given by Ruhemann (*loc. cit.*). It was converted into the *iso*nitroso derivative in the usual manner.

4:5-*Dimethoxy*-1:2-*diketohydrindene*.—The *iso*nitrosohydrindone (10 g.) was mixed with formaldehyde (20 c.c. of 40 %) and concentrated hydrochloric acid (5 c.c.) and heated to incipient boiling while being stirred. The *iso*nitroso compound passed into solution and the diketohydrindene separated as a crystalline powder The heating was continued for half an hour, the mixture cooled and diluted with water. The precipitated substance was collected, washed well with water and dried on the water-bath. It crystallised from benzene as yellow powder, m.p. 150° (decomp.). (Found: C, 63·9; H, 4·9. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·8 per cent).

4:5-*Dimethoxyindenoquinoxaline*.—1:2-Diketo-5:6-dimethoxyhydrindene (1 g.) and *o*-phenylenediamine (0·5 g.) were dissolved in hot ethyl alcohol. The crystalline product obtained on cooling the solution recrystallised from ethyl alcohol in slender needles, m p. 192°. (Found: C, 73·2; H, 5·3. $C_{17}H_{14}O_2N_2$ requires C, 73·4; H, 5·0 per cent).

2-*Carboxy*-5:6-*dimethoxyphenylacetonitrile*.— 4:5-Dimethoxy*iso*nitrosohydrindone (5 g.) dissolved in aqueous sodium hydroxide (53 c.c. of 10 %) was treated gradually with toluene-*p*-sulphonyl chloride (7 g.), solution being completed by heating the mixture on the steam-bath for 10 minutes. The cooled solution was filtered and the filtrate acidified with concentrated hydrochloric acid, when the carboxynitrile separated, yield 95 %. It crystallised from

dilute methyl alcohol, m.p. 175°. (Found: C, 59·9; H, 5·2. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0 per cent).

5:6-*Dimethoxyhomophthalic acid.*—The nitrile described above (10 g.) was hydrolysed with aqueous sodium hydroxide (100 c.c. of 10 %) for 5 hours on a sand-bath. The cooled solution was filtered and the filtrate acidified with concentrated hydrochloric acid, when 5:6-dimethoxyhomophthalic acid was precipitated in an yield of 90 %. It is sparingly soluble in cold water but fairly easily soluble in boiling water from which it crystallised in long needles, melting at 196°. (Found: C, 54·7; H, 5·2. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0 per cent).

5-Methoxy-1-hydrindone was prepared according to the method of Ingold and Pigott (*loc. cit.*).

5-*Methoxy*-iso*nitrosohydrindone.*—The ketone (5 g.) dissolved in methyl alcohol (15 c.c.) was mixed with freshly distilled *iso*amyl nitrite (7 c.c.) and concentrated hydrochloric acid (3 c.c.) and the mixture maintained at 50° for half an hour with vigorous stirring. The *iso*nitrosohydrindone separated in almost quantitative yield. It crystallised from alcohol in beautiful yellow needles, m.p. 221° (decomp.). (Found: C, 62·9; H, 4·6. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7 per cent).

5-*Methoxy*-1:2-*diketohydrindene* was prepared from the *iso*-nitrosohydrindone similarly as 4:5-dimethoxydiketohydrindene. It crystallised from benzene in needles, m.p. 152°. (Found: C, 67·8; H, 4·8. $C_{10}H_8O_3$ requires C, 68·1; H, 4·5 per cent).

5-*Methoxyindenoquinoxaline* was prepared in the same manner as 4:5-dimethoxyindenoquinoxaline and crystallised from alcohol, m.p. 140°. (Found: C, 77·4; H, 4·9. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·8 per cent).

2-*Carboxy-5-methoxyphenylacetonitrile* was prepared similarly as 2-carboxy-5:6-dimethoxyphenylacetonitrile, the yield being nearly quantitative. It crystallised from methyl alcohol in colourless needles, m.p. 177°. (Found: C, 62·6; H, 5·0. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7 per cent).

5-*Methoxyhomophthalic acid.*—This acid has been prepared by Ingold and Pigott (*loc. cit.*) by the direct oxidation of 5-methoxy-hydrindone with chromic acid. It is obtained more conveniently and in a better yield by the hydrolysis of 2-carboxy-5-methoxyphenyl-acetonitrile, m.p. 222°, yield 90 %.

6-*Methoxyhydrindone.*—This ketone has been prepared by Ingold and Pigott (*loc. cit.*) from the corresponding 6-nitrohydrindone

through the amino and hydroxy derivatives. Perkin and Robinson (*loc. cit.*) state that it is not formed in any appreciable amount by the action of aluminium chloride upon *p*-methoxyhydrocinnamoyl chloride and that it is formed in very small quantities by the action of P_2O_5 on the *p*-methoxyhydrocinnamic acid in benzene solution. After a series of experiments, it was found that 6-methoxyhydrindone could be directly prepared from *p*-methoxyhydrocinnamic acid in an yield of about 20% under the following conditions:— Aluminium chloride (10 g.) dissolved in nitrobenzene (50 c.c.) was gradually added during half an hour to a solution of *p*-methoxy-β-phenylpropionyl chloride (10 g.) in dry nitrobenzene (20 c.c.) (under cooling) and the whole allowed to remain overnight. The reaction product was decomposed with water and then subjected to steam distillation, when nitrobenzene first distilled over and then pure 6-methoxyhydrindone, m.p. 109°. It crystallised from alcohol in long needles, m p. 109°.

6-*Methoxy*iso*nitrosohydrindone*, prepared similarly as 5-methoxy-*iso*nitrosohydrindone, crystallised from alcohol in yellow needles, m. p. 234° (decomp.). (Found: C, 62·5 ; H, 4·9. $C_{10}H_9O_3N$ requires C, 62·8 ; H, 4·7 per cent).

6-*Methoxydiketohydrindene* is very soluble in the ordinary organic solvents and crystallised from ether in yellow plates, m. p. 126°. (Found: C, 68·0 ; H, 4·8. $C_{10}H_8O_3$ requires C, 68·1 ; H, 4·5 per cent).

6-*Methoxyindenoquinoxaline* crystallised from alcohol in silky needles, m. p. 156°. (Found: C, 77·4 ; H, 4·9. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·8 per cent).

4-*Methoxy-2-carboxyphenylacetonitrile* was prepared similarly as the isomeric 5-methoxy compound. It is more soluble in methyl alcohol than its isomer and crystallised in small needles, m. p. 140°. (Found: C, 62·6 ; H, 5·0. $C_{10}H_9O_3N$ requires C, 62·8 ; H, 4·7 per cent).

4-*Methoxyhomophthalic acid* was obtained by hydrolysing the above nitrile with aqueous sodium hydroxide and acidifying the alkaline liquid with concentrated hydrochloric acid. It crystallised from water in small needles, m. p. 183°. (Found: C, 57·5 ; H, 5·0. $C_{10}H_{10}O_5$ requires C, 57·1 ; H, 4·8 per cent).

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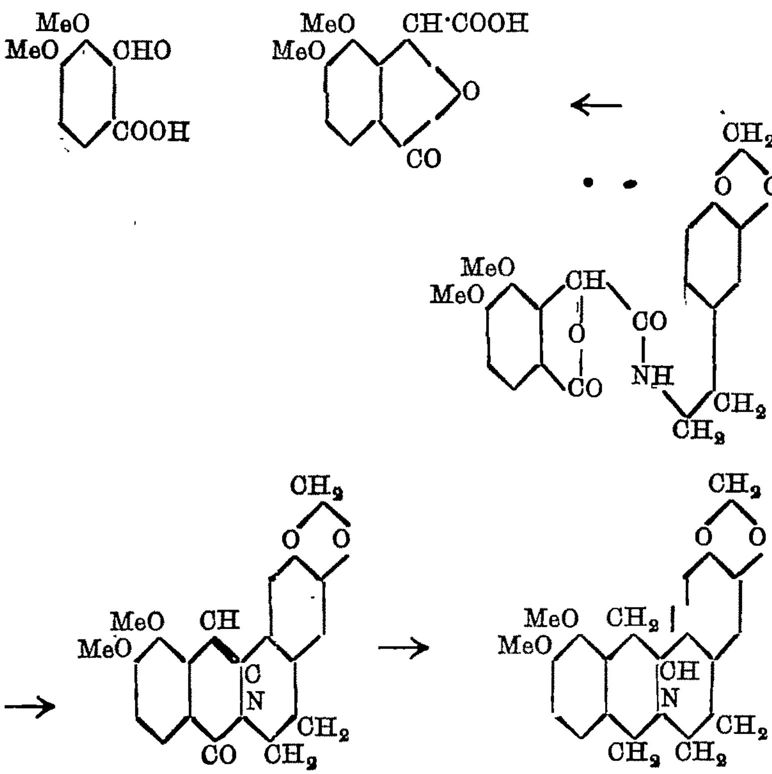
A Synthesis of 2:3-Methylenedioxy-11:12-dimethoxytetrahydroprotoberberine, an Isomer of Tetrahydroberberine and a Synthesis of 2:3:11:12-Tetramethoxytetrahydroprotoberberine, an Isomer of Tetrahydropalmatine.

By Satyendra Nath Chakravarti and M. Swaminathan.

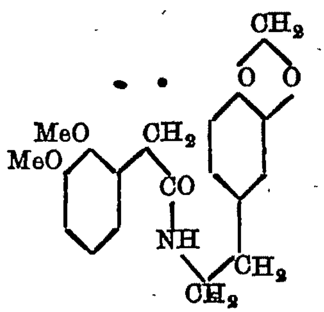
Berberine can be readily degraded to ψ-opianic acid through berberal (Perkin, *J. Chem. Soc.*, 1890, 57, 1002, Perkin and Robinson, *ibid.*, 1910, **97**, 321). It was, therefore, thought that it would be a matter of interest to synthesise an isomer of berberine by substituting ψ-opianic acid in place of opianic acid in the Perkin, Râу and Robinson synthesis of berberine (*J. Chem. Soc.*, 1925, **127**, 740), and compare the properties of the two alkaloids. The tetrahydro derivative of this isomer should have the constitution (II) as shown below :



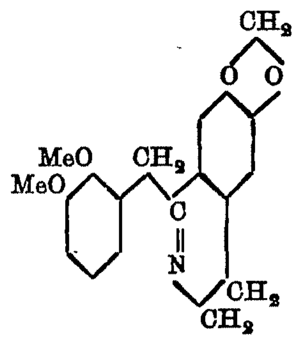
(I) (II)

ψ-Opianic acid being not yet readily available, this substance which may be called 2:3-methylene-dioxy-11:12:-dimethoxytetrahydroprotoberberine was synthesised in the following manner.

o-Veratraldehyde was condensed with hippuric acid and the azlactone hydrolysed to benzoic acid and 2:3-dimethoxyphenylpyruvic acid; the latter was then oxidised by hydrogen peroxide to 2:3-dimethoxyphenylacetic acid, which was condensed with β-piperonylethylamine and the 2:3-dimethoxyphenylaceto-β-piperonylethylamide (III) so obtained was converted in an yield of over 80% into a syrupy base. This base which is probably 6:7-methylenedioxy-1-(2: 3-methoxybenzyl)-3: 4-dihydro*iso*quinoline (IV) oxidizes rapidly on exposure to air and is readily reduced by zinc and sulphuric acid to 6:7-methylenedioxy-1-(2:3-methoxy benzyl)-1:2:3:4-tetrahydro*iso*quinoline (V), an oily base yielding a crystalline hydrochloride and picrate. Ring-closure of the formyl derivative was effected in the usual manner with phosphorus oxychloride and 2:3-methylenedioxy-11:12-dimethoxydihydroprotoberberine (VI) thus obtained, was immediately reduced to 2:3-methylenedioxy-11:12-dimethoxytetrahydroprotoberberine (II).



(III)



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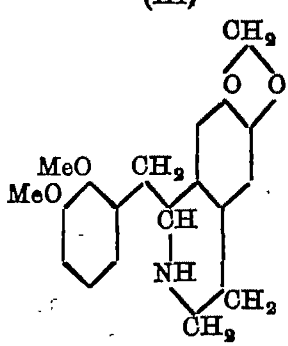

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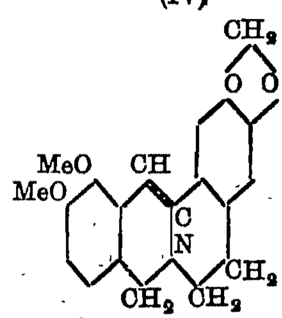
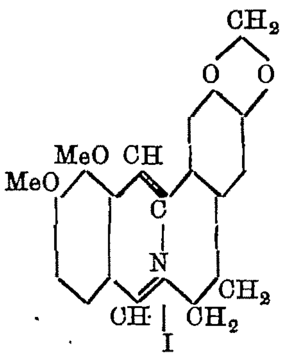


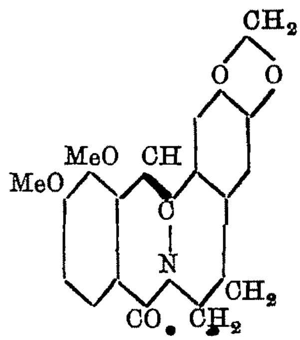
(VI)

It would be obvious from the formula (V) that ring-closure can take place only in one direction and the dihydroprotoberberine must have the formula (VI).

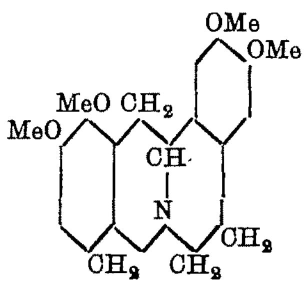
2 :3-Methylenedioxy-11 :12-dimethoxytetrahydroprotoberberine (II) is a colourless crystalline base, m.p. 127°. When it is oxidised with iodine in alcoholic solution, it yields 2 :3-methylenedioxy-11 :12-dimethoxyprotoberberinium iodide (VII) from which the corresponding chloride was prepared. The chloride is decomposed in the usual manner by potassium hydroxide giving 2 :3-methylenedioxy-11 :12-dimethyl-oxyprotoberberine (VIII) and dimethoxydihydroprotoberberine (VI) which are readily separated as the former is insoluble and the latter soluble in dilute mineral acids.



(VII)



(VIII)



(IX)

Next 2 :3 :11 :12-tetramethoxytetrahydroprotoberberine (IX), an isomer of tetrahydropalmatine was synthesised by a method similar to that outlined above in the case of (II). 2 :3-Dimethoxyphenylacetic acid condenses with β-veratrylethylamine to yield 2 :3-dimethoxyphenylaceto-β-veratrylethylamide (as III) which was converted first

into the dihydro*iso*quinoline (as IV), and then the latter reduced to 6:7-dimethoxy-1-(2:3-dimethoxybenzyl)-1:2:3:4-tetrahydro*iso*quinoline (as V), an oily base yielding crystalline salts. Ring-closure of the formyl derivative was effected in the usual manner with phosphorus oxychloride and 2:3:11:12-tetramethoxydihydroprotoberberine (as VI) thus obtained was immediately reduced to 2:3:-11:-12-tetramethoxytetrahydroprotoberberine (IX).

Experimental.

2:3-*Dimethoxyphenylacetic acid*.—This acid had been previously prepared from 2:3-dimethoxyphenylmandelonitrile (Heinrich and Krannichfeldt, *Ber.*, 1913, **46**, 4023). This acid is more conveniently prepared in the following manner.

o-Veratraldehyde was condensed with the hippuric acid in the presence of acetic anhydride and sodium acetate. The azlactone, m.p. 170° thus obtained was hydrolysed by means of 10% sodium hydroxide solution and the alkaline solution was then saturated with sulphur dioxide, the benzoic acid collected and the filtrate acidified with concentrated hydrochloric acid and boiled to decompose the bisulphite compound of the pyruvic acid, when 2:3-dimethoxyphenylpyruvic acid gradually separated in small needles, m.p. 145°. It was oxidised in cold alkaline solution with hydrogen peroxide. On acidifying the solution 2:3-dimethoxyphenylacetic acid, m.p. 84°, separated in an excellent yield. It crystallised from petroleum ether (b.p. 70-80°) in long beautiful needles.

2:3-*Dimethoxyphenylaceto-β-piperonylethylamide*.—Equivalent quantities of β-piperonylethylamine and 2:3-dimethoxyphenylacetic acid were heated at 180° for 2 hours. On crystallising the product from benzene, 2:3-dimethoxyphenylaceto-β-piperonylethylamide was obtained in colourless needles in a good yield, m.p. 108° (Found: C, 66·2; H, 6·0. $C_{19}H_{21}O_5N$ requires C, 66·5; H, 6·1 per cent).

6:7-*Methylenedioxy*-1-(2′:3′-*dimethoxybenzyl*)-1:2:3:4-*tetrahydroisoquinoline*.—The amide (10 g.) was heated with phosphorus oxychloride (25 c.c.) for 2 hours on the steam-bath and then kept overnight. The mixture was decomposed with cold water and the clear solution thus obtained was made alkaline in the presence of benzene in a separating funnel, the precipitate formed being immediately shaken up with benzene. The alkaline solution was once

more extracted with benzene. The benzene extract was again extracted with dilute sulphuric acid and the acid solution was reduced with zinc dust by heating on the steam-bath for 2 hours till the yellow colour disappeared. The solution was filtered hot and decomposed by means of ammonia and the tetrahydro base extracted with benzene, dried over potassium carbonate and the solvent removed, leaving the base as an oil. The hydrochloride, obtained by dissolving the oil in hot dilute hydrochloric acid and cooling, separated in small clusters of needles, m. p. 160°. (Found: C, 62·5 ; H, 6·2. $C_{19}H_{22}O_4NCl$ requires C, 62·7 ; H, 6·1 per cent).

2 : 3-*Methylenedioxy*-11 : 12-*dimethoxytetrahydroprotoberberine* was obtained in 50% yield by the following method. The tetrahydro*iso*quinoline was heated with equivalent amount of anhydrous formic acid in an oil-bath at 200° for 2 hours. The product was dissolved in toluene and boiled with phosphorus oxychloride for 1½ hours. After remaining overnight, light petroleum was added and the clear liquid decanted from the dark coloured gum, the latter extracted with dilute hydrochloric acid (charcoal) and the solution of dihydroprotoberberine reduced by heating with excess of zinc dust for 2 hours, during which the yellow solution became colourless. The hot liquid was filtered, the filtrate decomposed with ammonia, the base extracted with chloroform, dried over potassium carbonate, the chloroform removed and the residue crystallised from methyl alcohol. On recrystallisation from methyl alcohol (charcoal) the substance was obtained in beautiful needles, m. p. 127°. (Found : C, 70·5 ; H, 6·4. $C_{20}H_{21}O_4N$ requires C, 70·8 ; H, 6·2 per cent).

2 : 3-*Methylenedioxy*-11 : 12-*dimethoxyprotoberberinium iodide*.—2 : 3-Methylenedioxy-11 : 12-dimethoxytetrahydroprotoberberine (1·5 g.) dissolved in alcohol (50 c. c.) containing anhydrous sodium acetate (4 g.) was heated to boiling and a 2% alcoholic solution of iodine (150 c. c.) added slowly, when the periodide separated. After boiling for ½ hour, the whole was cooled and the crystals collected, suspended in boiling water and SO_2 was passed, when the iodide separated in yellow needles, m. p. 252°.

2 : 3-*Methylenedioxy*-11 : 12-*dimethoxyprotoberberinium chloride* was obtained by boiling an aqueous suspension of the iodide with excess of freshly precipitated silver chloride for 3 hours on the steam-bath. The filtrate was concentrated and treated with hydrochloric acid, when the chloride separated as yellow needles, m. p. 220°.

Oxy-2:3-methylenedioxy-11:12-dimethoxyprotoberberine.—A hot solution of the chloride (1·5 g) in water (15 c.c.) was added to a hot solution of KOH (6 g.) in water (25 c.c.) and the whole heated on the steam-bath for 3 hours. The yellow mass which separated was collected and extracted many times with boiling dilute hydrochloric acid. The insoluble residue crystallised from glacial acetic acid containing an equal volume of water as light yellow needles, m. p. 280-81°. (Found: C, 68·1; H, 5·0. $C_{20}H_{17}O_5N$ requires C, 68·4; H, 4·8 per cent).

On basifying the hydrochloric acid extract, the dihydroprotoberberine was precipitated. This substance is being further examined.

2:3-*Dimethoxyphenylaceto-β-veratrylethylamide* was prepared by heating together equivalent quantities of 2:3-dimethoxyphenylacetic acid and β-veratrylethylamine in an oil-bath at 180° for 2 hours. The product crystallised from benzene in colourless needles, m. p. 131°. (Found : C, 66·8 ; H, 7·0. $C_{20}H_{25}O_5N$ requires C, 66·9 ; H, 6·9 per cent).

6:7-*Dimethoxy*-1-(2′:3′-*dimethoxybenzyl*)-1:2:3:4-*tetrahydro*iso-*quinoline*.—The amide (10 g) was heated with phosphorus oxychloride (25 c.c) for 2 hours on the steam-bath and then kept overnight. The mixture was worked up in the same manner as in the previous case. The tetrahydro base was obtained as an oil which gave a crystalline hydrochloride, m. p. 204°, separating from dilute HCl in nodules. (Found : C, 63·6 ; H, 7·6. $C_{20}H_{26}O_4NCl$ requires C, 63·2 ; H, 7·3 per cent).

2:3:11:12-*Tetramethoxytetrahydroprotoberberine*.—(i) The tetrahydro*iso*quinoline was condensed in the presence of sodium bicarbonate with formaldehyde in methyl alcoholic solution. The condensation product which separated as a gum on the addition of water and some salt, was dissolved in concentrated hydrochloric acid and heated on the steam-bath for a few minutes. The acid solution gave with ammonia a base which crystallised from methyl alcohol in beautiful prisms, m. p. 163°.

(ii) This base was obtained in a better yield by the following method. The tetrahydro*iso*quinoline was heated with an equivalent amount of anhydrous formic acid in an oil-bath at 200° until effervescence had ceased (2 hours). The product was dissolved in toluene and boiled with phosphorus oxychloride for 1½ hours. After remaining overnight, light petroleum was added and the clear liquid decanted from the dark coloured gum, the latter extracted with dilute

hydrochloric acid (charcoal) and the solution of dihydroprotoberberine reduced by heating with excess of zinc dust for 2 hours on the steam-bath, when the yellow solution became colourless. The hot liquid was filtered and the filtrate decomposed with ammonia, the base extracted with chloroform, dried over potassium carbonate the chloroform removed and the residue crystallised from methyl alcohol. On recrystallisation from methyl alcohol, the substance was obtained in beautiful prisms, m. p. 168°. The mixed melting point of the products obtained by the two methods remained undepressed. (Found: C, 70·8 ; H, 7·1. $C_{21}H_{25}O_4N$ requires C, 71·0 ; H, 7·0 per cent).

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On the Study of Polyhalides. Part III.

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Various attempts have been made to determine the equilibrium relations existing between the polyhalides and their constituents in order to determine their constitution. That a tri-halide, such as that of potassium, barium, etc., may exist in solution is generally accepted. Many of the polyhalides, specially of the heavier alkali metals, have also been separated in the solid state. From measurements of conductivities, viscosities, migration numbers, distribution coefficients and other properties, usually over very limited range of concentrations, various authors have obtained indications of polyhalides to which, on more or less satisfactory grounds, they have been able to assign definite formulæ. References to the literature of the polyhalides of the alkali metals were given in the first part of this work (Ray, *J. Indian Chem. Soc.*, 1932, 9, 359). In order to obtain quantitative information of various polyhalides with different cations under the same condition and over a much wider range of concentrations of components than has yet been recorded, the present investigation was undertaken. The formation and dissociation of the chloro-dibromides, chloro-diiodides, bromo-diiodides and polybromides of sodium, potassium, strontium, barium, zinc and cadmium were studied at the temperature of 30° by the method of solubility.

The pure halide of definite concentration was shaken at a temperature of about 35°, with excess of iodine in well stoppered glass bottles for about 12 hours. It was then shaken in a thermostat kept at 30° until equilibrium was attained. Solutions were drawn off into pipettes through cotton wool plugs, any iodine removed by reaction with the cotton being negligible. Iodine was estimated by titration with $N/100$-sodium thiosulphate solution. The solubility of bromine in aqueous solutions of halides of different strengths was determined by shaking up excess of bromine with these solutions, contained in stoppered bottles as in the case of iodine. The bottles were shaken mechanically for 12 hours in a thermostat at 30°. The dissolved bromine in the solution was estimated indirectly, samples being removed by means of a pipette, introduced into excess of concentra-

ted potassium iodide solution and titrated with $N/2$-sodium thiosulphate solution. Special precautions were taken to prevent any loss of bromine during transference. Any change in the solubility of halogens in presence of different cations was neglected.

From the enhanced solubility of the halogens in the solutions of the chlorides and bromides of sodium, potassium, strontium, barium, zinc and cadmium, there appears to be little doubt that the increased solubility is due to combination of part of the dissolved halogen with the formation of polyhalides of the metals. Attempts to apply the mass action law in systems like these cannot be expected to succeed and there seems no reason to suppose that the formation of any one polyhalide represents the sole action at any particular concentration. However, in the cases of the chloro-dibromides and bromo-diiodides, over a certain range of concentrations, the values of the equilibrium constants calculated on the assumption that tri-halides are formed, are found to be fairly constant. The values of the equilibrium constants in the case of tri-bromo ions were always found to vary, the amount of bromine dissolved in these cases is much greater than that required for the formation of tri-bromo ions, specially in the more concentrated solutions of the bromides. Presumably in these cases higher polybromides, Br_5', Br_7', etc., are formed. Moreover, it appears that the tendency of the formation of higher polyhalides is the greatest in the case of polybromides and polyiodides as well. Further it will be seen from the values of the equilibrium constants that in the cases of the chloro-dibromides and chloro-diiodides of the alkali metals, the values remain constant only in dilute solutions, and diminishes greatly with increasing concentrations of the halide. The assumption of the formation of the tri-halides in these cases is only tenable over a very limited range of halide concentration above which higher polyhalides are also formed to a more or less extent. The values in the cases of the polyhalides of the divalent strontium, barium, zinc and cadmium are peculiar in as much as they remain constant only in fairly concentrated solutions, increasing to a very great extent with decreasing halide concentration. The values also show an increase in very concentrated solution as is evident from the Table VI. The cases of the divalent elements are somewhat complicated by the fact that in their cases the dissociation takes place by stages as suggested in Part II of this series (Ray, *J. Indian Chem. Soc.*, 1933, **10**, 213), as well as to the effect of hydrolysis of the halides on dilution.

The values of the equilibrium constants of the different poly-halides obtained by other investigators as well as by the author by different methods will be found in Part II of this work (*loc. cit.*).

The Formation of $ClBr_2$ *Ions.*

TABLE I.

Conc. of the halide in normality.	Formation of $NaClBr_2$. Solubility of Br in g./10 c.c. sat. solution.	Formation of $NaClBr_2$. Equilibrium constant *K*.	Formation of $KClBr_2$. Solubility of Br in g./10 c.c. sat. solution.	Formation of $KClBr_2$. Equilibrium constant *K*.
3	0·8187	1·812	0·9054	1·109
2	0·7485	1·471	0·8287	1·477
1	0·5692	1·544	0·6078	1·621
0·5	0·5057	2·414	0·5287	2·912
0·25	0·4362	3·184	0·4501	3·597
0·125	0·3774	3·188	0·3855	3·795
0·0625	0·3460	3·143	0·3501	3·758
0·0	0·3128	—	0·3128	—

TABLE II.

Conc. of the halide in normality.	Formation of $Sr_{\frac{1}{2}}ClBr_2$. Solubility of Br in g./10 c.c. sat. solution.	Formation of $Sr_{\frac{1}{2}}ClBr_2$. Equilibrium constant *K*.	Formation of $Ba_{\frac{1}{2}}ClBr_2$. Solubility of Br in g. /10 c.c. sat. solution.	Formation of $Ba_{\frac{1}{2}}ClBr_2$. Equilibrium constant *K*.
2	0·7491	2·176	0·7708	2·424
1·5	0·6839	2·152	0·6984	2·360
1	0·5886	2·141	0·6203	2·421
0·5	0·4714	2·258	0·4772	2·326
0·25	0·4020	2·215	0·4005	2·258
0·125	0·3615	2·390	0·3803	4·211
0·0625	0·3471	3·084	0·3600	7·532
0·03125	0·3326	4·109	0·3428	12·98
0·0	0·3128	—	0·3128	—

TABLE III.

Conc. of the halide in normality.	Formation of $Zn_{\frac{1}{2}}ClBr_2$. Solubility of Br in g./10 c.c. sat. solution.	Formation of $Zn_{\frac{1}{2}}ClBr_2$. Equilibrium constant K.	Formation of $Cd_{\frac{1}{2}}ClBr_2$. Solubility of Br in g./10 c.c. sat. solution.	Formation of $Cd_{\frac{1}{2}}ClBr_2$. Equilibrium constant K.
2	0·6102	1·750	0·4813	2·008
1·5	0·5669	1·786	0·4296	2·043
1	0·5264	1·827	0·4065	2·042
0·5	0·4395	1·848	0·3765	2·039
0·25	0·3861	1·888	0·3587	2·070
0·125	0·3529	1·919	0·3410	2·322
0·0625	0·3340	1·903	0·3301	2·414
0·0	0·3128	—	0·3128	—

The Formation of ClI_2 *Ions.*

TABLE IV.

Conc. of the halide in normality.	Formation of $NaClI_2$. Solubility of I in g./25 c.c. sat. solution.	Formation of $NaClI_2$. Equilibrium constant K.	Formation of $KClI_2$. Solubility of I in g./25 c.c. sat. solution.	Formation of $KClI_2$. Equilibrium constant K.
3	0·03263	1·455	0·03448	1·201
2	0·03077	1·542	0·03120	1·493
1	0·02244	1·831	0·02394	2·078
0·5	0·01671	1·824	0·01819	2·094
0·25	0·01352	1·804	0·01436	2·150
0·125	0·01183	1·827	0·01205	2·190
0·0625	0·01094	1·868	0·01173	2·243
0·0	0·00991	—	0·00991	—

TABLE V.

Conc. of the halide in normality.	Formation of $Sr_{\frac{1}{2}}\ OII_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $Sr_{\frac{1}{2}}\ OII_2$. Equilibrium constant K.	Formation of $Ba_{\frac{1}{2}}\ OII_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $Ba_{\frac{1}{2}}\ OII_2$. Equilibrium constant K.
2	0·02576	1·768	0·02614	1·886
1·5	0·02318	1·717	0·02389	1·857
1	0·02017	1·780	0·02114	1·908
0·5	0·01609	1·915	0·01678	2·118
0·25	0·01388	2·248	0·01598	2·914
0·125	0·01221	2·458	0·01296	3·272
0·0625	0·01124	2·713	0·01157	3·406
0·0	0·009886	—	0·009886	—

TABLE VI.

Conc. of the halide in normality.	Formation of $Zn_{\frac{1}{2}}\ OII_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $Zn_{\frac{1}{2}}\ OII_2$. Equilibrium constant K.	Formation of $Cd_{\frac{1}{2}}\ OII_2$. Solubility of I in g./25 c.c. sat. solution.	Formation of $Cd_{\frac{1}{2}}\ OII_2$. Equilibrium constant K.
6	0·02943	2·342	0·01811	3·815
4	0·02771	2·130	0·01743	2·841
2	0·02157	1·620	0·01438	1·671
1·5	0·01962	1·506	0·01411	1·652
1	0·01744	1·496	0·01330	1·662
0·5	0·01441	1·515	0·01281	1·714
0·25	0·01288	1·933	0·01207	2·353
0·125	0·01199	2·303	0·01168	3·179
0·0625	0·01119	2·601	0·01091	3·042
0·0	0·009886	—	0·009886	—

The Formation of BrI_2 *Ions.*

TABLE VII.

Conc. of the halide in normality.	Formation of $NaBrI_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $NaBrI_2$. Equilibrium constant K.	Formation of $KBrI_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $KBrI_2$. Equilibrium constant K.
4	0·3257	17·23	0·3603	16·97
3	0·2580	15·37	0·2818	14·94
2	0·1911	14·74	0·1966	13·25
1	0·1076	13·86	0·1053	12·47
0·5	0·06107	13·79	0·05952	12·48
0·25	0·03628	13·76	0·03015	12·49
0·125	0·02457	14·23	0·02375	13·06
0·0625	0·01865	16·54	0·01750	13·96
0·0	0·00991	—	0·00991	—

Solubility of iodine in various concentrations of sodium bromide and potassium bromide at 25° was studied by Bell and Buckley (*J. Amer. Chem. Soc.*, 1912, **34**, 10).

TABLE VIII.

Conc. of the halide in normality.	Formation of $Sr_{\frac{1}{2}}BrI_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $Sr_{\frac{1}{2}}BrI_2$. Equilibrium constant K.	Formation of $Ba_{\frac{1}{2}}BrI_2$. Solubility of I in g./25 c. c. sat. solution.	Formation of $Ba_{\frac{1}{2}}BrI_2$. Equilibrium constant K.
2	0·1606	15·57	0·1501	14·62
1·5	0·1393	15·40	0·1270	14·64
1	0·1051	15·60	0·0959	14·72
0·5	0·06299	15·87	0·06004	15·17
0·25	0·03836	15·83	0·03805	15·77
0·125	0·02892	16·50	0·02522	15·99
0·0625	0·01852	16·32	0·01895	16·08
0·0	0·009836	—	0·009836	—

TABLE IX.

Formation of $Cd_{\frac{1}{2}}BrI_2$.

Conc. of the halide in normality	Solubility of I in g./25 c.c. sat. solution.	Equilibrium constant K.
2	0·4896	18·16
1	0·4050	17·46
0·5	0·3080	17·49
0·25	0·2368	17·68
0·125	0·1844	17·72
0·0625	0·1501	18·62
0·0	0·0991	

Solubility of Bromine in Bromide Solutions.

From the solubility of bromine in the solutions of the bromides of sodium, potassium, strontium, barium and cadmium, the formation of the tri-bromides of the metals cannot be confirmed; the values of the equilibrium constants are found to vary to a great extent even in very dilute solutions, while in concentrated solutions the amount of bromine dissolved is much greater than that required for the formation of the tri-bromides. In the fairly concentrated solutions, on the other hand, the values of equilibrium constants, calculated on the assumption of the formation of the penta-bromide, are found to give a better result though the values are never constant. It is assumed that in these cases, a mixture of both tri-bromides and penta-bromides and even some higher polybromides are always formed to a more or less extent.

TABLE X.

Solubility of bromine in NaBr *and* KBr.

Conc. of the halide in normality.	Solubility of Br in g./10 c.c. sat. solution of NaBr.	KBr.
4	8·127	—
3	4·861	6·013
2	2·458	4·117
1	1·150	2·031
0·5	0·7325	1·144
0·25	0·5137	0·7513
0·125	0·4032	0·5201
0·0625	—	0·4858
0·0	0·3123	0·3123

TABLE XI.

Solubility of bromine in $SrBr_2$ *and* $BaBr_2$.

Conc. of the halide in normality.	Solubility of Br in g./10 c.c. sat. solution of $SrBr_2$.	$BaBr_2$.
2	3·024	3·181
1·5	2·596	2·527
1	2·009	2·111
0·5	0·9785	1·034
0·25	0·7003	0·7114
0·125	0·4371	0·4410
0·0625	0·3835	0·3901
0·0	0·3123	0·3123

The solubility of bromine in NaBr of various strengths at 25° was studied by Bell and Buckley (*loc. cit*). The solubility of bromine in KBr was studied by the following investigators.

Temp.	Authors.	Reference.
0° and 25°	Boericke	*Z. Electrochem.*, 1905, **11**, 57
18·5° and 26·5°	Worley	*J. Chem. Soc.*, 1905, **87**, 1107
0°	Jones and Hartmann	*J. Amer. Chem. Soc.*, 1916, **37**, 241

TABLE XII.

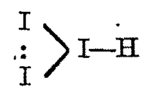
Solubility of Bromine in $CdBr_2$.

Conc. of the halide (*N*)	2	1	0·5	0·25	0·125	0·0625	0·0
Solubility of Br_2 g./per 10 c.c. sat. soln.	1·319	1·003	0·8674	0·5845	0·4656	0·4295	0·3128

It will be seen from the preceeding tables that the values of the equilibrium constants of any particular polyhalogen ion vary with the nature of the cations as pointed out in Part II of this work (*loc. cit.*). The order of variation as previously found in the cases of sodium and potassium is also found to be the same in the present investigation. The cases of the divalent elements strontium, barium, zinc and cadmium are also found to be analogous to that of the monovalent elements, sodium and potassium. Here also the volume of the cation plays the same part in governing the reaction; zinc having the least of ionic radius exerts the greatest influence and barium with the greatest radius have the least effect. But there appears to exist no relation between the monovalent and the divalent series. The value of the equilibrium constant of $NaClBr_2$ is greater than the corresponding value of $Ba_{\frac{1}{2}}ClBr_2$; the ionic volume of barium being greater than that of sodium, the reverse was expected in their cases. This anomaly is to be attributed to the doubly positive charge on the barium ion, the increase of charge being much greater than the increase in radius, the attracting force is much more pronounced in the case of the doubly charged divalent elements.

The constitution of these polyhalides is a matter of much controversy. From the electrical conductivity and the lowering of the freezing point as shown by Schmidt (*Z. anorg. Chem.*, 1895, **9**, 431), Sullivan (*Z. physikal. Chem.*, 1899, **28**, 523), Jakovkin (*ibid.*,

1894, 13, 539) and Ephraim (*Ber.*, 1917, 50, 1069) it was suggested that the constitution agrees with the assumption that the tri-iodides are the salts of hydrotriiodic acid, HI_3, with tervalent iodine atoms:

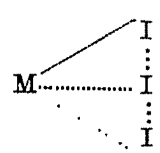


Werner ("Neuve Anschaungen auf dem Gebiete der anorganischen Chemie", Leipzig, 1913) regards the tri-halides as addition compounds, so that the tri-halide $RICl_2$ becomes $\left[Cl \cdot I \cdot Cl\right] R$, dichloro-iodates on his system of nomenclature. The penta-halides are tetrachloro-iodates analogous to the chloroaurates:

$$\left[\begin{array}{ccc} & Cl & \\ Cl & .\,\dot{Au}. & Cl \\ & \dot{Cl} & \end{array}\right] \qquad \left[\begin{array}{ccc} & Cl & \\ Cl\ . & \dot{I} & .\ Cl \\ & \dot{Cl} & \end{array}\right]$$

Werner says that the hepta and ennea halides can be explained on the assumption that the co-ordinated positions are occupied by iodine molecules. The non-existence of the tri-chlorides, after Werner " is to be attributed to chlorine being unable to act as a central atom".

According to Ephraim ("Text Book of Inorganic Chemistry", Eng. Trans., 1926, p. 260) the constitution of these polyhalides is not very clear. The iodine molecule may be added on to the iodine ion as indicated thus: $I\,(I)_2$ or the additional iodine may be more closely attached to the metal thus:



This formula according to him does not indicate an increase in valency of the metal but only a subdivision of its valency. It was also suggested by him that the property of forming polyiodides is connected with the volume of the cation.

None of these formulae explain the general properties of the polyhalides, specially the extreme unstable nature of many of them. The singlet electron linkage as suggested by Cremer and Duncan (*J. Chem. Soc.*, 1933, 181) explains to a certain extent the unstability of

these compounds but the singlet electron linkage theory itself is controversial and in these series of compounds seems to be inadmissible. It is unlikely that the original stable linkage between the atoms of the halogen molecule should be ruptured and a new rather unstable bond should be formed in its place as is required by the assumption of Cremer and Duncan (*loc. cit.*). The author is of the opinion that in these compounds the union is of an electrostatic nature, the charge on the halogen ion causes a displacement of the positive and negative charges in the neutral halogen molecule, so that it becomes polarised; the two being held together by the electrostatic attraction between the negative charge on the halogen ion and the induced opposite charge on the neutral molecule as suggested in Part II of this work (*loc. cit.*). This conception of the electrostatic combination explains the unstability of these compounds satisfactorily while it is the only assumption that can explain the influence of cations on the reactions leading to the formation of the polyhalides (Ray, *loc. cit.*).

Summary.

By means of solubility, the formation of polyhalides of sodium, potassium, strontium, barium, zinc and cadmium have been confirmed and their dissociation constant at 30° determined and the constitution of the polyhalides has been discussed.

My grateful thanks are due to Prof. P. R. Rây of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest they took in the work.

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Compounds of Hexamethylene Tetramine with Complex Cobalt Salts and the Nature of Residual Affinity.

BY PRIYADARANJAN RÂY AND MANINDRACHANDRA BAKSHI.

Hexamethylene tetramine has been found to combine with a large number of salts and acids, both simple and complex, to form molecular or additive compounds. Several investigators have worked on the subject and a complete reference thereto will be found in Ray and Sarkar's paper (*J. Chem. Soc.*, 1921, **119**, 390). The substance has also been employed as a microchemical reagent (Vivario and Wagennar, *Pharm. Weekbl.*, 1917, **54**, 157; *Z. anal. Chem.*, 1919, **58**, 228; 1925, **67**, 298). Rây and Sarkar (*Mikrochem. Emich Festschrift*, 1930, p. 243) have already shown that magnesium and other alkaline earth salts readily give with several complex metallic cyanides and urotropine characteristic crystals, suitable for microchemical identification of the corresponding alkaline earth element. The composition of these compounds thus formed was not determined by the authors. In the present paper the preparation, properties and the composition of the molecular compounds, formed by urotropine with several simple and double salts of thiosulphato-pentacyano-cobaltic acid, have been described. The alkali and alkaline earth salts of this acid have been prepared by Rây and his co-workers (*J. Indian Chem. Soc.*, 1927, **4**, 325; *Z. anorg. Chem.*, 1931, **199**, 353). The compositions of the compounds prepared, together with those of the original salts, are given in Table I.

TABLE I.

$X = [(CN)_5.Co.S_2O_3]''''$ and $B = C_6H_{12}N_4$.

Original salt.	Compounds with urotropine.	Diff. in H_2O mols.
Ba_2X, 7·5 H_2O	Ba_2X, 1·5B, 4·5 H_2O	−3
Sr_2X, 3·5 H_2O	Sr_2X, 2B, 7H_2O	3·5
Ca_2X, 8 H_2O	Ca_2X, 2B, 8H_2O	0
Mg_2X, 9·5 H_2O	Mg_2X, 2B, 12 H_2O	2·5
Li_4X, 4 H_2O	Li_4X, 2B, 8 H_2O	4
—	BaK_2X, 1·5B, 1·5H_2O	—
—	SrK_2X, 1·5 B	—
—	CaK_2X, B, 7 H_2O	—
—	MgK_2X, 2B, 2·5 H_2O	—
—	Li_2K_2X, 2B	—
—	$Ba(NH_4)_2X$, 1·5B, 4·5 H_2O	—
—	$Sr(NH_4)_2X$, 1·5B, 2 H_2O	—
—	$Ca(NH_4)_2X$, B, 7H_2O	—
—	$Mg(NH_4)_2X$, 1·5B, 5H_2O	—

The double alkali-alkaline earth salts of the complex acid have not been described ; but the addition of urotropine to a solution of the alkali salt of the complex acid in presence of any alkaline earth salt precipitates the compounds of the double alkali-alkaline earth salt of the complex acid with the base. Similar compounds of urotropine with complex ferro- and ferricyanides have been described by Barbieri (*Gazzetta,* 1930, **60**, 229). The composition of these compounds as well as of the original complex cyanides are also shown below.

TABLE II.

$X = [Fe(CN)_6]$ and $B = C_6H_{12}N_4$.

Original salt.	Compounds with urotropine.	Diff. in H_2O mols.
$Mg_2X, 10H_2O$	$Mg_2X, B, 12H_2O$	2
MgK_2X	$MgK_2X, B, 8H_2O$	8
$Mg(NH_4)X$	$Mg(NH_4)_2X, B, 10H_2O$	10
$MgNa_2X$	$MgNa_2X, B, 9H_2O$	9
$Sr_3X_2, 14H_2O$	$Sr_3X_2, 4B, 20H_2O$	6
$Sr(NH_4)X, 3H_2O$	$Sr(NH_4)X, 2B, 5H_2O$	2
$SrKX, 3H_2O$	$SrKX, 2B, 5H_2O$	2
$Ca_3X_2, 12H_2O$	$Ca_3X_2, 4B, 20H_2O$	8
$CaKX, 3H_2O$	$CaKX, 2B, 6H_2O$	3
$Ba_3X_2, 20H_2O$	$Ba_3X_2, 3B, 18H_2O$	—2
K_3X	$K_3X, B, 9H_2O$	9 Rây & Sarkar (*loc. cit.*)
$K_3Co(CN)_6$	$K_3Co(CN)_6, B, 6{\cdot}5 H_2O$	6·5 ,,

An examination of the composition of these compounds with those of the original salts reveals many interesting features regarding the nature of secondary valencies as exhibited in these molecular compounds. In most cases it will be observed that the capacity for association with water molecules for any particular salt increases after combination with hexamethylene tetramine, though one would naturally expect that the satisfaction of residual valencies by the addition of the latter would reduce the number of water molecules in the products formed. The point of association of the hexamine molecules, or, for the matter of that, of water molecules, in the addition

compounds cannot, therefore, be definitely localised. Thus, for example, potassium ferricyanide and hexamine both crystallise out from water in the anhydrous state. But when mixed together, they form the addition compound of the formula $K_3Fe(CN)_6,C_6H_{12}N_4,9H_2O$. If we assume that the water molecules are attached to the positive ion, the point of attachment of the hexamine molecules becomes indefinite. It cannot be attached to the central atom of the anion which is co-ordinatively saturated. Barbieri, (*loc. cit.*) therefore, suggests that the hexamine molecules do not associate directly with the anions or cations, but combine with the salt by an indirect secondary valency in the sense meant by Werner and Weinland. Nor there is any justification to assume that the water molecules are attached to the positive ion or even to the hexamine molecule, as both the original salt and urotropine are anhydrous. Similar arguments apply equally to the cases of other compounds, where the addition of hexamine raises the water content of the product. The only plausible interpretation under these circumstances is that the hexamine molecules, which very likely possess fairly well developed dipole moments like ammonia, are held by electrostatic attraction to the positive and negative ions of the salt. This may, under certain circumstances, give rise to an alteration in the electrical field around the ions, whereby their capacity for associating dipole molecules of water is increased. In other words, both hexamine and water molecules are held simply by electrostatic attraction of the ions of the salt ; no secondary valency of directional character, consisting of shared electrons as suggested by some, takes any part in the formation of these molecular or additive compounds.

EXPERIMENTAL.

Compounds of Urotropine with Simple and Double Salts of Thiosulphato-pentacyano-cobaltic Acid.

Barium salt and urotropine.—A moderately strong solution of hexamethylene tetramine was added drop by drop to a concentrated solution of thiosulphato-pentacyano barium cobaltiate with constant stirring in the cold (0°). Beautiful golden yellow crystals readily separated out. The crystals were filtered, washed with 10% urotropine solution and then with aqueous alcohol (1:1), and finally with

absolute alcohol. These were then dried in the air. The crystals readily dissolve in water giving orange coloured solution. (Found: N, 17·54; Ba, 31·12; Co, 6·93. $Ba_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $1{\cdot}5(CH_2)_6N_4$, $4{\cdot}5H_2O$ requires N, 17·77; Ba, 31·7; Co, 6·8 per cent).

Strontium salt and urotropine.—A slight excess of saturated solution of hexamine was added little by little with constant stirring to the solution of strontium salt of the complex cobaltic acid. The compound was obtained as a yellowish crystalline precipitate which was then drained, washed and dried as in the previous case. The crystals are very soluble in water, and, when examined under the microscope, appear as rectangular prisms and bars. (Found: N, 20·46; Co, 6·7; Sr. 19·86. $Sr_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, 2 $(CH_2)_6N_4$, $7H_2O$ requires N, 20·63; Co, 6·7; Sr, 19·86 per cent).

Calcium salt and urotropine.—The substance was prepared from a saturated solution of the calcium salt and a moderately concentrated solution of hexamine in the same way as the previous compounds. The pale yellow crystals separating were filtered, washed and dried as before. The crystals are very soluble in water and appear as plates and crosses under the microscope. (Found: N, 22·28; Ca, 10·01; Co, 7·33. $Ca_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $2(CH_2)_6N_4$, $8H_2O$ requires N, 22·63; Ca, 9·94; Co, 7·33 per cent).

Magnesium salt and urotropine.—The substance was prepared from a concentrated solution of thiosulphato-pentacyano magnesium cobaltiate and a moderately strong solution of urotropine as in the case of previous compounds. The double compound was obtained as a light-yellow crystalline precipitate. The crystals were washed and dried as usual. (Found: N, 21·5; Co, 6·99; Mg, 5·85. $Mg_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, 2 $(CH_2)_6N_4$, $12H_2O$ requires N, 21·41; Co, 6·94; Mg, 5·75 per cent).

Lithium salt and urotropine.—The thiosulphato-pentacyano lithiumcobaltiate was dissolved in the least amount of water. It was cooled in ice, then to this was added drop by drop a saturated solution of urotropine with constant stirring until the hexamine was in slight excess. The mixure was afterwards treated with 2-3 drops of alcohol. The crystals separated were drained, washed at first with 50 % alcohol, then with absolute alcohol and finally dried in air. The light-yellow crystalline substance appears as bushes of needles under the microscope. (Found: N, 24·27; Co, 7·75; Li, 3·78. $Li_4[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $2(CH_2)_6N_4$, 8 H_2O requires N, 24·2; Co, 7·33; Li, 3·81 per cent).

Barium potassium salt and urotropine.—A saturated solution of thiosulphato-pentacyano potassium cabaltiate (6 g.) was mixed with requisite amount of barium chloride (1·28 g.) and a little potassium chloride (0·2 g) solution. On adding urotropine solution to the mixture, while constantly stirring, a light-yellow crystalline substance separated. It was drained, washed with aqueous urotropine (5%) until free from chloride, then with 5% alcohol and lastly with absolute alcohol. The substance was finally dried in air. It is less soluble in water than the pure barium compound. When examined under the microscope, it was found to consist of octahedral crystals. (Found: N, 20·57; Ba, 18·28; Co, 7·85; K, 10·38. $BaK_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $1{\cdot}5(CH_2)_6N_4$, $1{\cdot}5H_2O$ requires N, 20·45; Ba, 18·2; Co, 7·83; K, 10·36 per cent).

Strontium potassium salt and urotropine.—Thiosulphato-pentacyano potassium cobaltiate (3 g.), strontium chloride (0·5 g.) and a little potassium chloride were dissolved in the least quantity of water. The solution was then treated drop by drop with a concentrated solution of hexamine in slight excess. Yellow crystals of the double compound separated at once. These were filtered, washed and dried as in the previous case. The crystals appeared octahedral in shape under the microscope. (Found: N, 23·2; Co, 8·72; K, 11·55; Sr, 12·94. $SrK_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $1{\cdot}5(CH_2)_6N_4$ requires N, 22·8; Co, 8·71; K, 11·52; Sr, 12·94 per cent).

Calcium potassium salt and urotropine.—Calcium chloride (1 g.), the complex potassium salt (5 g.), and potassium chloride (0·5 g.) were dissolved in the least quantity of water. The mixture was placed in ice, and urotropine solution was added to it drop by drop with constant stirring until it was in slight excess. Light yellow crystals separated at once. It was filtered, washed and dried as before. The crystals, under the microscope, appear as rhombohedral plates. (Found: N, 18·54; Ca, 5·9 ; Co, 8·66 ; K, 11·45· $CaK_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $(CH_2)_6N_4$, $7H_2O$ requires N,18·4; Ca, 5·83; Co, 8·61; K, 11·38 per cent).

Magnesium potassium salt and urotropine.—The complex potassium salt (4 g.) was dissolved in the least amount of water ; requisite amount of $MgSO_4$ (1 g.) and a little KCl (0·5 g.) were added to this solution. The cooled solution was mixed with urotropine while being constantly stirred. The substance separated out in yellow crystals. These were then dried and washed as before. The crystals appear as bushes of needles under the microscope.

(Found: N, 24·78; Co, 8·04; K, 10·62; Mg, 3·58. $MgK_2 [(CN)_5 \cdot Co \cdot S_2O_3]$, $2(CH_2)_6N_4$, 2·5 H_2O requires N, 24·97; Co, 8·08; K,10·7; Mg,3·33 per cent).

Lithium potassium salt and urotropine.—A mixture of 5·4 g. of thiosulphato-pentacyano potassium cobaltiate, 0·12 g. of lithium chloride and 0·5 g. of potassium chloride was dissolved in the least amount of water and filtered. The clear filtrate was treated in the cold with a concentrated solution of urotropine in slight excess. The yellow crystalline precipitate formed was filtered, washed and dried as usual. The crystals appeared under the microscope octahedral in shape. (Found: N, 26·67; Co, 8·83; K, 11·49; Li, 2·03. $Li_2K_2 [(CN)_5 \cdot Co \cdot S_2O_3]$, 2 $(CH_2)_6N_4$ requires N, 27·0; Co, 8·76; K, 11·59; Li, 2·08 per cent).

Barium ammonium salt and urotropine.—The complex ammonium salt (4 g.), $BaCl_2$ (0·5 g.) and NH_4Cl (0·2 g.) were dissolved in the least amount of water. The mixture was cooled in ice and mixed with a little excess of a concentrated solution of hexamine with constant stirring. Beautiful golden yellow crystals separated readily. These were filtered, washed and dried as in the previous cases. The compound is very soluble in water, and appears as prismatic rods under the microscope. (Found: N, 23·71; Ba, 17·95; Co, 7·75. $Ba(NH_4)_2[(CN)_5 \cdot Co \cdot S_2O_3]$, $1{\cdot}5(CH_2)_6N_4$, $4{\cdot}5H_2O$ requires N, 23·71; Ba, 17·94; Co, 7·71 per cent).

Strontium ammonium salt and urotropine.—The substance was prepared in the same way as the previous compounds from the complex ammonium salt, ammonium chloride, strontium chloride and hexamine. The substance, which consists of light yellow crystals, is extremely soluble in water, and appears under the microscope as rhombic plates. (Found: N, 26·74; Co, 8·74; Sr, 12·88. $Sr (NH_4)_2 [(CN)_5 \cdot Co \cdot S_2 O_3]$, 1·5 $(CH_2)_6 N_4$, $2H_2O$ requires N,27·1; Co, 8·80; Sr, 13·05 per cent).

Calcium ammonium salt and urotropine.—The compound was prepared from the complex ammonium salt, ammonium chloride, calcium chloride and urotropine in a way similar to that of the previous compound. The light-yellow crystals obtained were washed and dried as usual. Under the microscope the crystals appear octahedral in shape. (Found: N, 28·91; Ca, 6·20; Co, 8·96. $Ca(NH_4)_2[(CN)_5 \cdot Co \cdot S_2O_3]$, $(CH_2)_6N_4$, $7H_2O$ requires N, 28·95; Ca, 6·22; Co, 9·12 per cent).

Magnesium ammonium salt and urotropine.—The substance was prepared from the complex ammonium salt, magnesium sulphate, ammonium sulphate and urotropine. The details of the preparation are identical with those of the previous compound. The yellow crystals obtained were filtered, washed and dried as before. These appear to consist of tetragonal plates under the microscope. (Found: N, 27·82; Co, 8·85; Mg, 3·66. $Mg(NH_4)_2[(CN)_5{\cdot}Co{\cdot}S_2O_3]$, $1{\cdot}5(CH_2)_6N_4$, $5H_2O$ requires N, 27·53; Co, 8·92; Mg, 3·67 per cent).

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Studies in the Coagulation of Colloids. Part VII. Some Anomalous Variations of Viscosity during the Coagulation of Ferric Hydroxide and Antimony Sulphide Sols.

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In previous parts of this series (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329 ; Joshi and Menon, *ibid.*, 1933, **10**, 599) it was shown that an initial diminution followed by a rise of viscosity, and the existence of breaks in the viscosity—time curves were the conspicuous features of the *slow* coagulations of arsenious sulphide and gelatine sols (both when free and mixed together) in the presence of the solutions of a number of electrolytes, the strength of the sol and of the coagulator being varied over a suitable range in each series. Since the existence of both these phenomena has an important bearing both on the general theory of the viscosity of colloids and of the coagulation process, and since with the exception of the above work from these laboratories, practically no information is available in the literature in this line, it was thought desirable to extend the above results to coagulations of some other sols.

Experimental.

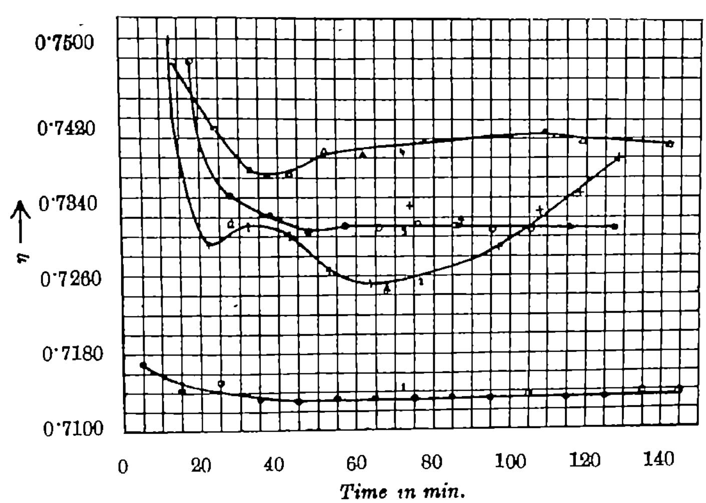
The method of measuring the viscosity and the general experimental procedure were the same as those adopted previously (*loc. cit.*). The values for the colloid and the coagulator concentration refer to those before mixing. The measurement of the viscosity was discontinued only after *flocculation* had set in. The temperature of the thermostat was kept constant at $35° \pm 1°$ in all the experiments. 30 C.c. of the coagulating mixture were used. It contained 20 c.c. of the sol and 10 c.c. of the appropriate electrolyte solution, except in No. 1, Table I, when 10 c.c. of water only were added to the colloid. All these liquids were allowed to attain the thermostat temperature before mixing in the viscometer. The constancy of the

pressure observed on the manometer (*cf.* Fig. A, Part V, Joshi and Viswanath, *loc. cit.*) applied to the viscometer was judged by means of a low power telescope.

During the course of preliminary experiments it was observed that a *freshly dried* viscometer always indicated a higher viscosity in the first observation. By examining this phenomenon under different conditions it was found that even with pure water the apparent viscosity in the initial observation could be as high as 2 % when the viscometer was highly desiccated by a prolonged current of hot and well dried air passed through it. This factor, however, could be eliminated by measuring the viscosity after the capillary and the bulb of the viscometer were once wetted by the liquid in the viscometer. In the following experiments, therefore, the viscometer was well wetted by the colloid before measurements of the viscosity of the coagulating mixture were commenced.

The kinetics of the coagulation of two colloids, *viz.*, ferric oxide and antimony sulphide were examined viscometrically and the results were similar to those in Part V (Joshi and Viswanath, *loc. cit.*). The ferric oxide sol was prepared by hydrolysing a solution containing about 5 g. of ferric chloride per litre by prolonged boiling and then dialysing it for 20 days. The dialysate was found to be free of chlorine after

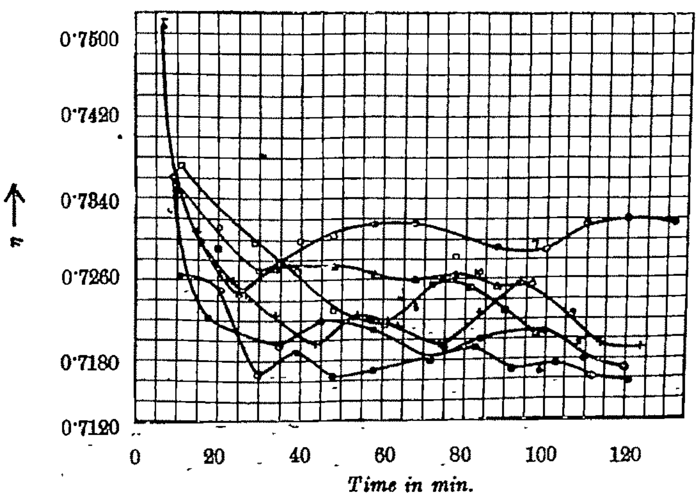
FIG. 1. (*cf.* TABLE I).



Curve 1 refers to water and Fe_2O_3 sol. Curves 2—4 refer to Fe_2O_3 sol + 0·0002, 0·001 and 0·002 *N*-KCl respectively.

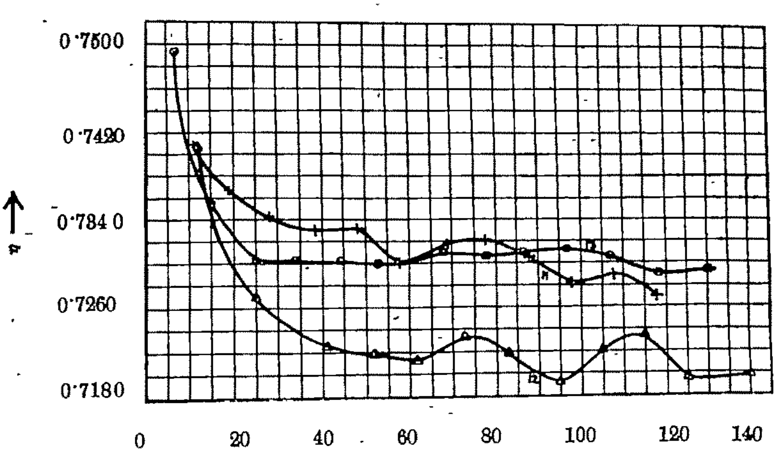
this period. The colloid content of the sol was determined by coagulating a known amount of the sol by a barium chloride solution and then weighing the coagulum. It was 1·95 g. of Fe_2O_3 per litre. The viscosity variations during its coagulation by solutions of potassium chloride, barium chloride, ferric chloride and thorium nitrate are shown in Figs. 1—4 (*cf.* Tables I—IV). The antimony

FIG. 2. (*cf.* TABLE II).



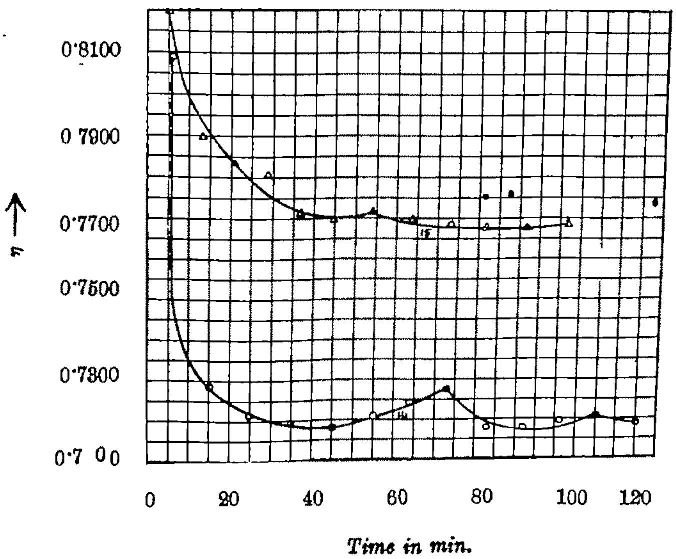
Curves 5—10 refer to Fe_2O_3 sol + 0·0025, 0·005, 0·01, 0·02, 0·05 and 0·1*N*-$BaCl_2$ respectively.

FIG. 3. (*cf.* TABLE III).



Curves 11—13 refer to Fe_2O_3 sol + 0·01, 0·0˝, and 0·1*N*-$FeCl_3$ respectively.

FIG. 4. (*cf.* TABLE IV).



Curves 14—15 refer to Fe_2O_3 sol + 0·1 and 1·0*N*-$Th(NO_3)_4$ respectively.

sulphide sol was prepared as in an earlier paper (Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, 8, 11). It was dialysed for 12 days against repeated changes of hot water and was found free of acid. A portion of this sol was diluted with water and used in the experiments with thorium nitrate (Fig. 8 also Table VIII). The other portion of the sol was dialysed for 14 days longer, and used in coagulations by solutions of potassium chloride, potassium tartrate and potassium oxalate (Figs. 5—7; Tables V—VII). The concentrations of these sols, determined as in the case of colloid ferric oxide, were respectively, 2·05 and 1·45 g. of Sb_2S_3 per litre. The data in the 4th column of Tables I—VIII show η, the viscosity in centipoise units at the first minimum observed on the η—time curves. The time corresponding to this minimum is shown in the next column. As observed previously, the η—time curves were discontinuous. In order to give an idea of the magnitude of these discontinuities only one pair of points, which are *widest* apart on the η-axis of each curve, is considered, *e.g.*, points *a* and *b* on curve 2, Fig. 1. The mean of the difference between the viscosities corresponding to *a* and *b*, is expressed as a percentage of the *initial* viscosity. These results are given in the 9th column of Tables I—VIII.

The following abbreviations have been used in the following tables:

C = concentration of electrolytes; η_i = initial viscosity in centipoise; η_m = first minimum viscosity; $T\eta_m$ = time corresponding to η_m; η_d = viscosity decrease; η_f = final observed viscosity; $T\eta_f$ = time corresponding to η_f; R = range of fluctuation of η.

TABLE I (*cf.* Fig. 1).

Fe_2O_3 sol + water.

Ref. curve No.	C.	η_i.	η_m.	$T\eta_m$.	η_d.	η_f.	$T\eta_f$.	R.	Remarks.
1		0·717	0·713	45	0·6%	0·713	145		

Fe_2O_3 sol + KCl.

Ref. curve No.	C.	η_i.	η_m.	$T\eta_m$.	η_d.	η_f.	$T\eta_f$.	R.	Remarks.
2	0·0002N	0·750	0·729	22	2·8%	0·733	120	0·4%	No flocculation.
3	0·0010	0·748	0·731	43	2·3	0·731	128	—	Do
4	0·0020	0·748	0·736	43	1·6	0·739	128	0·2	Flocculates.

TABLE II (*cf.* Fig. 2).

Fe_2O_3 sol + $BaCl_2$.

Ref. curve No.	C.	η_i.	η_m.	$T\eta_m$.	η_d.	η_f.	$T\eta_f$.	R.	Remarks.
5	0·0025N	0·736	0·719	35	2·3%	0·717	120	0·3%	No flocculation.
6	0·0050	0·726	0·717	30	1·2	0·716	121	0·2	Do
7	0·0100	0·735	0·727	30	1·1	0·731	132	0·2	Opalescent after 30′.
8	0·0200	0·737	0·721	60	2·2	0·720	98	0·6	Opalescent after 20′. Flocculates after 98′.
9	0·0500	0·751	0·720	44	4·1	0·719	104	0·2	Opalescent after 15′. Flocculates after 44′. Coagulates after 104′.
10	0·1000	0·751	0·725	25	3·5	0·725	98	0·3	Opalescent immediately. Flocculates after 48′. Coagulates completely after 88′.

TABLE III (*cf.* Fig. 3).

Fe_2O_3 sol + $FeCl_3$.

Ref. curve No.	C.	η_i.	η_m.	$T\eta_m$.	η_d.	η_f.	$T\eta_f$.	R.	Remarks.
11	0·01N	0·741	0·730	88	1·5%	0·730	213	0·1%	No flocculation.
12	0·05	0·741	0·721	62	2·7	0·720	140	—	Do
13	0·10	0·749	0·730	53	2·5	0·730	130	0·3	Opalescent after 39′. Flocculates after 97′.

TABLE IV (*cf.* Fig. 4).

Fe_2O_2 sol + $Th(NO_3)_4$.

Ref.	*C.*	η_i	η_m.	$T\eta_m$.	η_d.	η_f.	$T\eta_f$.	E.	Remarks.
14	0·10*N*	0·809	0·721	25	10·9%	0·719	120	—	No flocculation.
15	1·00	0·819	0·770	45	6·0	0·768	102	0·2%	Opalescent immediately. Flocculates after 64′. Coagulates completely after 102′.

TABLE (V. *cf.* Fig. 5).

Sb_2S_3 sol + KCl.

1	0·001*N*	0·749	0·740	16	1·2%	0·760	116	—	No flocculation.
2	0·005	0·745	0·738	17	0·9	0·790	137	—	Do
3	0·010	0·756	0·741	26	2·0	0·834	126	1·3%	Do
4	0·020	0·752	...	...	...	0·851	125	0·6	Do
5	0·030	0·753	...	...	...	0·951	44	26·0	Opalescent after 24′. Flocculates after 44′.
6	0·050	0·764	...	...	...	1·190	39	53·0	Opalescent after 17′. Flocculates after 39′.

TABLE VI (*cf.* Fig. 6).

Sb_2S_3 sol + $K_2C_2O_4$.

7	0·010*N*	0·760	0·737	24	3·0%	0·741	114	0·3%	No flocculation.
8	0·025	0·754	0·734	18	2·7	0·750	118	0·3	Do
9	0·040	0·757	0·743	35	1·9	0·753	125	1·7	Do
10	0·050	0·754	...	...	...	1·448	87	...	Opalescent after 48′. Flocculates after 87′.

TABLE VII (*cf.* Fig. 7).

Sb_2S_3 sol + $K_2C_4H_4O_6$.

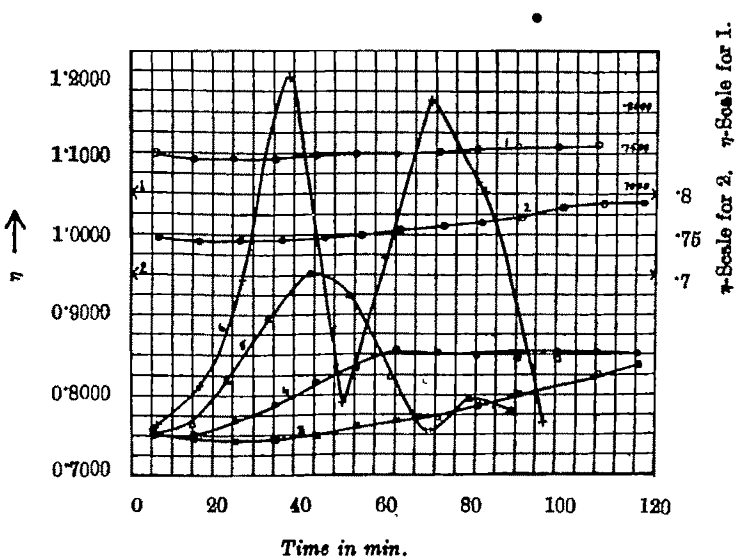
11	0·020*N*	0·742	0·728	25	1·9%	0·726	114	0·4%	No flocculation.
12	0·040	0·748	0·729	26	2·5	0·730	126	0·3	Do
13	0·050	0·752	...	...	...	0·821	129	...	Opalescent after 59′. Flocculates after 129′.
14	0·060	0·753	...	...	...	1·026	82	...	Opalescent after 24′. Flocculates after 70′.

TABLE VIII (*cf.* Fig. 8).

Sb_2S_3 sol + Th $(NO_3)_4$.

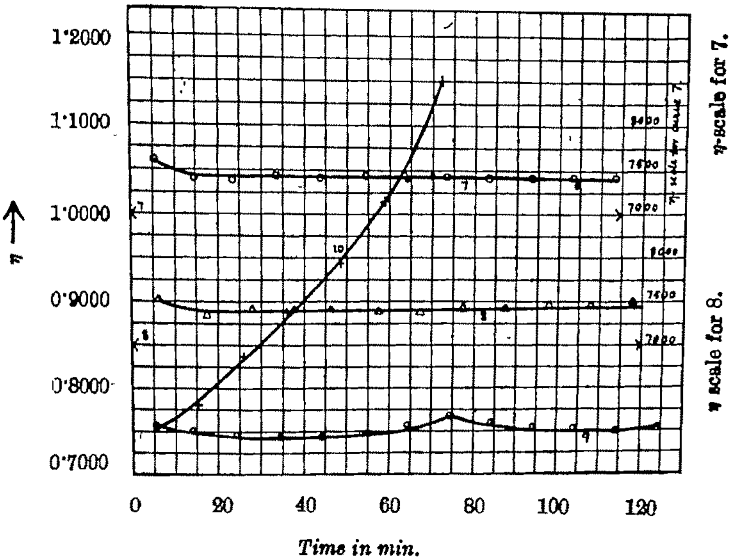
Ref.	C.	η_i.	η_m.	Tη_m.	η_d.	η_f.	Tη_f.	R.	Remarks.
15	0·001*N*	0·726	...	...	...	0·728	125	0·5%	No flocculation.
16	0·002	0·736	0·725	16	·1·1%	0·732	116	0·3	Do
17	0·003	0·722	...	...	...	0·731	122	0·5	Do
18	0·004	0·731	0·725	61	0·8	0·727	129	0·3	Do
19	0·005	0·738	0·732	85	0·8	0·740	125	0·6	Do
20	0·006	0·739	...	...	...	0·760	161	1·0	Opalescent after 96′ Flocculates after 122′.

FIG. 5 (*cf.* TABLE V).



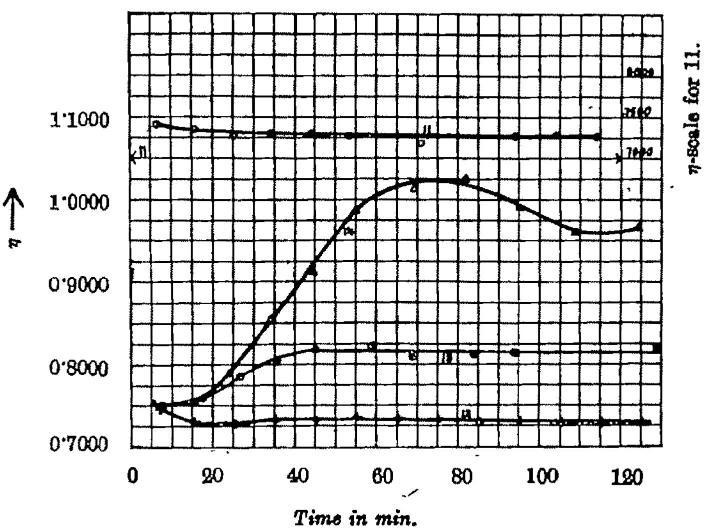
Curves 1—4 refer to Sb_2S_3 sol + 0·001, 0·005, 0·01, 0·02, 0·03, and 0·05*N*-KCl respectively.

FIG. 6 (*cf.* TABLE VI).



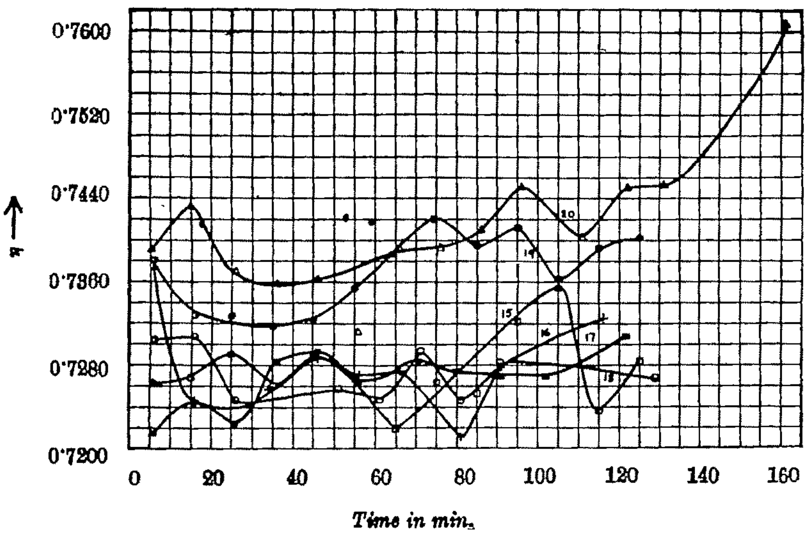
Curves 7—10 refer to Sb_2S_3 sol + 0·01, 0·025, 0·04 and 0·05N-$K_2C_2O_4$ respectively.

FIG. 7. (*cf.* TABLE VII).



Curves 11—14 refer to Sb_2S_3 sol + 0·02, 0·04, 0·05 and 0·06N $K_2C_4H_4O_6$ respectively.

FIG. 8. (*cf.* TABLE VIII).



Curves 15—20 refer to Sb_2S_3 sol + 0·001, 0·002, 0·003, 0·004, 0·005 and 0·006*N*-Th $(NO_3)_4$ respectively.

DISCUSSION.

An examination of the curves in Fig. 1—8 gives ample support to the deduction made previously (Parts V, VI) that in so far as the viscosity is a measure of coagulation, at least in the *slow* region, the coagulation (in the sense of a sustained coalescence of particles) is not a continuous process in respect of time. As has been observed previously (*loc. cit.*), in a number of cases, *e.g.*, curves 3—6 in Fig. 5, curves 12—14 in Fig. 7 are 'S-shaped' showing a slow initial change followed by a more rapid one. In general this is ascribed to *autocatalysis*. This is not strictly valid since the existence of discontinuities on η—time curves might also be interpreted as showing that a viscosity change is not a measure of coagulation. It is instructive to consider the influence of the electrolyte concentration revealed by the curves in Fgs. 5 and 7 for the antimony sulphide sol. The S-shaped part of the curve becomes progressively steeper as the strength of the electrolyte solution is increased. Moreover, at very low values of the last, when practically the entire η—time curve is a part of the S-shape, there are hardly any marked discontinuities. These are more pronounced at higher concentrations (*cf.* curves 5, 6, Fig. 5), *wherewith only*, coagulation was observed to

progress sensibly as judged by opalescence and the setting in of flocculation (*cf.* Table V). This shows clearly that the discontinuities are *a part* of the mechanism of the coagulation of polydisperse sols, at any rate in the *slow* region. It might also be pointed out that the almost constancy of the viscosity (subsequent to the initial stage) where coagulation was either nil (*cf.* curve 1, Fig. 1) or had a very low rate of progress (*cf.* curves 11—13, Fig. 7; curves 1—3, Fig. 6) shows that the breaks in such curves as 5 and 6 in Fig. 5, where coagulation was most rapid, cannot be ascribed to any experimental error. This source would also appear to be improbable in view of the fact that the η-fluctuations on these curves are as high as 26 and 58 % (*cf.* Table V). It was previously observed (Part VI) that breaks were rather more frequent in coagulations due to thorium nitrate than when other electrolytes were used. This agrees with our present results (*cf.* Fig. 8). Curves 15—18 in this figure do not show any appreciable net increase of viscosity. This is sensible in curves 19 and especially in 20 in Fig. 8. These represent the largest concentration of the electrolytes, *viz.*, thorium nitrate in this series That coagulation was just appreciable only in the last case is shown. by the evidence of opalescence and flocculations (*cf.* Table VIII). Considering the *overall* trend of the curve, it is seen to be **S**-shaped and it has also *discontinuities*. This is markedly different from the curves in Figs. 5—7 corresponding to the use of other coagulants where for the same sol, the **S**-parts of the η-time curves are sensibly free from discontinuities. It would thus appear that in the *slow* region the occurrence and the extent of these discontinuities depend upon the nature both of the colloid and of coagulator, and very likely also on the stage of the coagulation. Compared with η—time curves obtained in Part V for different series of coagulations, the initial viscosity diminution and the subsequent section of the curves, now observed for the coagulations of the antimony sulphide sol, are less pronounced. This is mainly due to the different scale used in plotting the results. The initial viscosity diminution now observed varies in the range 0·8—3 % of the initial viscosity and it is produced during 16 – 61 minutes after the commencement of the coagulation (*cf.* Tables V—VIII). On comparison, it will be seen that these quantities are similar to those reported previously in Parts V and VI (*loc. cit.*).

An outstanding feature of the viscosity—time curves (Fgs. 1—4) for the coagulation of the ferric hydroxide sol is that the change

is accompanied by a diminution of viscosity. This is contrary to the general experience, *viz.* that coagulation produces an increase in the viscosity of a sol. These curves (Figs. 1—4) also show that decrease of viscosity becomes more pronounced in the order KCl $\lessdot$ $BaCl_2$ < $FeCl_3$ < Th $(NO_3)_4$. It is interesting to consider the viscosity diminution at the first minimum in these η-time ovrves (*cf.* columns 6, Tables I—IV). This varies from 1-10 % of the initial viscosity, about 3 % being the average value. The time corresponding to this occurrence lies in the range of 20-60 minutes after the start of the coagulation. Work is now in progress in these laboratories to investigate as to how far this viscosity diminution is similar to that observed in the case of the coagulation of the antimony sulphide sol studied, here and of other sols referred to in Parts V and VI.

SUMMARY.

Slow coagulations of colloid ferric oxide due to variously concentrated KCl, $BaCl_2$, $FeCl_3$ and $Th(NO_3)_4$ and of antimony sulphide by KCl, $K_2C_2O_4$, $K_2C_4H_4O_6$ and $Th(NO_3)_4$ solutions have been studied by measurement of the viscosity with time. As observed previously in parts V and VI, in a number of coagulations of the latter sol, the η—time curves show an initial fall of 0·8 to 3 % of initial viscosity during 16—61 minutes after the start of coagulation. The next section usually possesses 'S-shape' whose duration diminishes as the electrolyte concentration is increased. The η—time curves show a number of breaks which are considered to indicate that in the *slow* region the coagulation is not a time-continuous process. Contrary to the general experience of the coagulation phenomena, in the case of the Fe_2O_3 the coagulation was accompanied by a diminution of η, the effect increasing in the order, KCl$\lessdot$ $BaCl_2$$\lessdot$ $FeCl_3$$\lessdot$ Th $(NO_3)_4$.

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BENARES.

Received October 30, 1933.

OBITUARY

JNANENDRA MOHON DAS-GUPTA, M.Sc.

Born. February, 1905. Died, 4th January, 1934.

Jnanendra Mohon Das-Gupta was born in 1905 at Dacca. He belonged to a Hindu Baidya family. He passed his matriculation examination from Noakhali and secured a divisional scholarship. He graduated from St. Xavier's College, Calcutta, with First Class Honours in Chemistry and secured a First Class M.Sc. degree in chemistry from Dacca University in 1923. As a research chemist in 1927 he joined the Brahmachari Research Institute and conducted original research work on the pharmaceutical chemistry under the able guidance of Rai Bahadur Dr. U. N. Brahmachari, with whose collaboration he published the following papers in the Journal of the Indian Chemical Society in 1931 and 1932.

Studies in Quinoline Compounds. Parts IV, VI and VII.

The following independent papers of Mr. Jnanendra Mohon Das-Gupta were published in the Journal of the Indian Chemical Society in 1933 and 34.

Studies in the decomposition and reactions of Urea. Parts I to IV.

In October 1933, he proceeded to Edinburgh with a view to carry on further research work on pharmaceutical chemistry in Edinburgh University under Professor Barger where he died of pneumonia.

He was elected a Fellow of the Society in 1930.

Chemical Aspects of Carbon Assimilation.*

By Prof. Nil Ratan Dhar, D.Sc., Dr. es. Sc., F.I.C.

I thank you most heartily for the honour you have done me by electing me your President. When just twelve years ago the leading chemists and some distinguished physicists of our country brought to me at Madras as the President of the Chemical Section of the Indian Science Congress, an application requesting me to take steps for the formation of an Indian Chemical Society and a strong committee with the late Dr. E. R. Watson as chairman was appointed, I was doubtful whether the country would realise the importance of the steps that we were taking in founding an Indian Chemical Society. It is a matter of extreme satisfaction to all of us that in the short period of twelve years, the Indian Chemical Society is a well organised, learned institution with a fairly large membership and an important Journal, the success of which goes to the friendly co-operation of Indian Chemists of all sections and to the generosity of the Calcutta University for printing it free of cost. The most pressing need of the Society seems to be the increase in the number of Fellows and the collection of donations from our Fellows as well as from industrial magnates and others concerned with the progress of the country, for increasing the permanent fund of the Society.

There is one more topic concerning our Society on which I venture to say a few words. Sometimes it has heen urged that there is unnecessary delay in the publication of papers, which under our rules have to be carefully scrutinised by at least two competent authorities on the subject matter of the paper. If I may state my own experience, frequently papers written by me have been criticised and improvements suggested by referees, and I have generally found that the papers have improved by the alterations put forward. I beg of authors of papers to put up with the criticisms of the referees and alter their presentation according to the suggestions made by the

* Presidential address for the Tenth Annual General Meeting of the Indian Chemical Society at Bombay, Jan. 1934.

referees, and I am sure of the majority of cases, the papers will improve in presentation.

Following the practice of my predecessors, I shall discuss from the chemical view-point one of the most fundamental problems of science in which chemists, botanists, physiologists, and agriculturists have taken a considerable interest and a problem on which our life on this earth depends. I mean the production of food and fuel from carbonic acid. The importance of this problem has long been realised.

Introduction.

The following conversation is said to have passed between Stephenson, the famous discoverer and engineer and Buckland, the celebrated geologist when they watched a railway train vanish rapidly in the distance.

" Well, Buckland," said Stephenson as he looked at the famous geologist, " what is it that drives the yonder train along? "

" Well," answered the geologist, " I should think that it is one of your great engines."

" Yes, but what moves the engine? "

" Why, one of your Newcastles engineers".

" No, sunlight."

" How can that be ?" asked the geologist.

" I assure you it is nothing else " replied the engineer.

" It is light that has been stored in the earth for many thousands of years ; the light absorbed by the plant during its growth is essential for the condensation of carbon, and this light which has been hidden in the coal for so many years, is now unearthed and being set free as in this engine, serves human beings."

The organic compounds synthesised by the plants are partly used up by them for their own food, but the greater part of these energy-rich organic substances, which are products of their labour are stored in their own bodies. A small part of this stored up materials is required for and used up as seeds and thus succeeding generations of plant life continue on the earth's surface. The majority of the energy-producing compounds manufactured by plant is, however, used by animals for their existence.

It appears, therefore, that in plants, in presence of sunlight the preparation of food materials and the consumption of a portion of the manufactured food can go on simultaneously. Animals, however,

consume the food manufactured by the plants and cannot produce their own nutrients in their body like the plants. Hence from this point of view, plant machinery is superior to that of the animal.

From times immemorial men came to the conclusion that all energy must ultimately come to us from the sun and therefore sun was worshipped as the All Father, the Giver of all good. The sun is the source of all our wealth, power and life. The radiation from the sun amouuts to more than 8 $\times 10^{33}$ calories per year. Of this amount the earth only receives 188 $\times 10^{22}$ calories.

It is estimated that the plants convert per year sixty billion kilograms of carbon dioxide to useful organic substances. It has been calculated that only 1/10,000 part of the total solar energy received on the surface of the earth is utilised in the formation of useful organic substances.

In this connection the following observations of L. J. Henderson are of interest :—" Two chemical individuals stand alone in importance for the great biological cycle upon earth. The one is water, the other carbon dioxide. These two simple substances are the common sources of every one of the complicated substances which are produced by living beings and they are the common end-products of the wearing away of all the constituents of the protoplasm and of the destruction of those materials which yield energy to the body".

It is clear, therefore, that life on the earth rests on the energy obtained from the sun through the phenomenon of photosynthesis going on in plants. Man depends entirely on this solar energy, which is made available to him by agricultural pursuits.

In photosynthesis, nature has evolved a method of storing the energy of the sun and it is the only photochemical change known in which energy is stored up for the use of mankind.

Efficiency of Carbon Assimilation not High.

Uufortunately the efficiency of this most important chemical change is not of a high order. Pütter (1914) found that about 3% of the solar energy is utilised by various crops. Oats use 3·31%, potatoes 3·02%, beets 2·12%, wheat 3·26%, and barely from 2·6 to 3·68%. According to Miller (1928), only 2·2% of the total radiation falling on an acre of land in Kansas (U. S. A.) under field conditions is utilised by corn for carbohydrate formation.

History.

Priestley (1778) and Scheele, who are discoverers of oxygen gas, also independently and simultaneously studied the problem of carbon assimilation, but their conclusions were diametrically opposite. While Priestley's plants improved the air rendered unfit by the animals, Scheele's plants produced carbon dioxide, because neither Priestley nor Scheele realised the importance of light in these experiments. Ingen-Housz (1779-1796) discovered the importance of light in this reaction and seems to have realised the cosmical function of green plants aided by sunlight and the relation between plant and animal nutrition. Senebier (1783-1800) appears to be the first to show that evolution of oxygen by plants in sunlight is accompanied by the absorption of CO_2 and not that of air. He also observed that it was not the solar heat but light, which causes the liberation of CO_2 in plants. Moreover, he was also the first to show that the red part of the solar spectrum was most active in the decomposition of carbonic acid. De Saussure (1804), who was highly influenced by Lavoisier's quantitative studies, introduced quantitative observations in this subject and came to the conclusion from rather crude experiments that the volume of oxygen evolved by plants is the same as that of carbon dioxide absorbed. He observed that the plants gain in weight by the intake of carbonic acid gas. He definitely established that carbon dioxide was absolutely necessary for the growth of plants from experiments carried on with plants kept in a confined space from which carbon dioxide was removed by potassium hydroxide. He showed that the plants died under these conditions, and also observed that oxygen is necessary for plant life and in an atmosphere of nitrogen and carbon dioxide plants cannot live. The importance of water in photosynthesis was also recognised by de Saussure. He appears to have introduced the idea of photosynthetic and respiratory quotients. Hence he extended our knowledge on this subject considerably, chiefly as a result of his quantitative methods.

Although Priestley, Ingen-Housz, Senebier and de Saussure believed that the green parts of the plant were active in the absorption of carbon dioxide and liberation of oxygen, Dutrochet in 1867 established the fact that the presence of chlorophyll in the green parts of the plants was responsible for the assimilation of carbon dioxide. In numerous publications Liebig (1840) was the first to

emphasise that carbon dioxide present in the air formed the only source of carbon for the plant life. It will, however, be shown later on that plants absorb carbon dioxide from the soil as well as from the atmosphere. Although the researches of von Mohl (1851) and Unger (1855) were important in showing that carbohydrates are the first substances to be produced in photosynthesis, Sachs (1862) was the pioneer to show that starch was the first visible product formed by the plant leaf from carbon dioxide absorption. This great botanist was also the first to make the important observation that when leaves rich in starch are placed in the dark, they lose starch. It appears again when the starch-free leaves receive light. Later on, Meyer (1885) showed that there is a group of plants *e.g.*, *Asclepias cornuti* and many *Monocotyledons*, most *Compositæ*, *Umbelliferæ*, etc., which do not form starch but sugars in photosynthesis. Hence starch need not always be the first visible product of photosynthesis as advocated by Sachs.

The crude experiments of de Saussure were considerably improved by the great agricultural chemist Bossingault (1864), but his conclusions were the same as that of de Saussure regarding the ratio of the volume of carbon dioxide absorbed and oxygen evolved. The chemical change involved in carbon assimilation is usually represented by the following equation:

$$6CO_2 + 6H_2O + 660{,}000 \text{ cal} = C_6H_{12}O_6 + 6O_2.$$

Actual Velocities of Carbon Assimilation.

Blackman asd Miss Matthaei (1905) obained the following results with *Helianthus tuberosus*. In brilliant August sunshine at Cambridge, at a temperature varying from 29·8° to 31° in an atmosphere containing 6·3% carbon dioxide, the assimilation was 0·022 g. of CO_2 for 50 sq. cm. of leaf surface and 5·8 g. of CO_2 per sq. m. of the leaf surface per hour. Willstätter and Stoll (1918) reported that 8 g. of CO_2 per sq. m. of the leaf surface with *Helianthus annus* and 6·3 g. for the same surface and temperature with *Cucurbita pepo* are absorbed. These results of Willstätter and Stoll are the highest values of carbon assimilation obtained so far under artificial conditions. Miller (1917) has stated that the average velocity of carbon assimilation in air during a period of ten hours for pumkin, cow peas and soy beans corresponds to 1·8, 0·85 and 0·8 mg. carbohydrate per hour per sq. dcm. of the leaf surface. The velocity for *pumkin* as observed by Miller

is practically the same as that obtained by Sachs (1884) for *Helianthus annuus.* Working with *Hydrilla,* Sir J. C. Bose obtained the value 28 mg. per sq. dcm. of leaf surface per hour; this is the maximum rate observed by Sir J. C. Bose. These velocities of carbon assimilation are much less than those obtained by Blackman and Matthaei and Willstätter and Stoll and others under artificial conditions using much larger concentrations of carbon dioxide.

It is of interest to note that the velocity of photosynthesis in Philippine Islands with leaves of sugar cane, cocoanut, etc., is reported by McLean (1920) to be small and the maximum absorption of carbon dioxide by sugar cane leaves corresponds to 0·35 mg. of carbohydrate per sq. dcm. per hour under natural conditions. It appears likely that the high temperature in the Philippine Islands causes a marked acceleration of respiration and hence the velocity of photosynthesis appears to be small. It seems, therefore, that in tropical countries photosynthesis need not be high even when the light intensity is large, because of the increase of respiration, which opposes photosynthesis.

Influence of the Concentration of Carbon Dioxide on Carbon Assimilation and some Practical Applications.

Warburg (1922), from careful experiments on the unicellular alga, *Chlorella,* kept at 25°, and exposed to radiations from a metal filament lamp giving out light of intensity greater than that of direct sunlight, has concluded that at low concentrations of carbon dioxide, the velocity of photosynthesis is almost directly proportional to the carbon dioxide content (concentration of CO_2 from 1/120 to 10 times the normal amounts present in air). When the concentration of CO_2 is greater than 2×10^{-6} mol. per litre, increase in the concentration of CO_2 causes a smaller increase in the velocity of photosynthesis. In the final stages of the concentration, the velocity of photosynthesis seems to be independent of CO_2 concentration.

Harder (1921) has studied this problem with aquatic plants much more systematically and has come to the conclusion that the higher the light intensity the greater will be the increasing effect of an enhancement of carbon dioxide concentration. Lundegärdh's experiments (1924) with land plants show that when the light intensity is $\frac{1}{40}$th of that of sunlight, an increase in photosynthetic

velocity is observed when the carbon dioxide concentration is increased and it is above normal. The increase in photosynthetic rate at pressures slightly exceeding the normal pressures is high but falls off as the concentration of carbon dioxide is increased. On the other hand, when the light intensity approaches that of sunlight, the photosynthetic velocities are greatly increased by an increase in the concentration of carbon dioxide.

In recent years attempts have been made to increase the yield of a crop by increasing the carbon dioxide concentation in the atmosphere surrounding the plants. Demoussy (1904) was the first to observe that plants grown in an atmosphere enriched in carbon dioxide showed an increase of 157·6% in excess of the control plants which were exposed to an atmosphere of normal carbon dioxide content, whilst the other plants had an atmosphere containing carbon dioxide to the extent of 0·15 to 0·18% for nearly two months. Kostyschew (1922) has reported that legumes are more affected by increase of CO_2 concentration than non-leguminous plants. Careful experiments carried on in Sweden by Lundegärdh (1924) in glass houses in which CO_2 was continuously passed, gave the following results for plants grown for 10 weeks.

	CO_2 house.	Control house.	Excess.	
Cucumber—shoots	1·1807 kg.	0·890 kg.	0·917 kg.	103%
Tomatoes—shoots	2·700	1·310	1·390	124
Bean fruits	7·080	3 343	3·737	112
Mean CO_2 content	0·0650%	0·043%	0·022%	51

Similar results were obtained by Fischer, Riedel, Jess, Owen and others. Although the results depend on the fertility of the soil and climatic conditions, they appear to be of great importance from the view point of practical agriculture. The artificial increase of carbon assimilation by an increase of CO_2 is possible by the nearness of big factories, which produce large amounts of CO_2 (the Krupp factories at Essen generate about 3000,000 kg. CO_2 per day). In this connection the following lines from Maximov's Plant Physiology (1930) will be of interest:

"The rapid development of the plants in hot beds underlaid with manure seems to be due not only to the high temperature thus produced, but also the abundant supply of carbon dioxide."

Soil as a Source of Carbon Dioxide for Plants.

"Under natural conditions plants obtain CO_2 not only from the atmosphere, but also from the soil. Due to the processes of decomposition of the organic substances in the soil by different micro-organisms, CO_2 is liberated. Diffusing from the soil in the lower layers of the atmosphere, it is caught by the leaves of the plants. According to the calculations of Lundegärdh, a sandy soil, poor in humus, liberates about 2 kg. of CO_2 per hour per hectare, while loam and clay soils containing a greater amount of humus, eliminate about 4 kg. and forest soils, extremely rich in humus, produce from 10 to 5 kg. Moderately fertillized soils produce on an average 5 kg. of CO_2 per hectre per hour. A field of one hectare sown to oats consumes in the process of photosynthesis about 15 kg. of CO_2 per hour. Five of these are supplied by the soil; the other ten are obtained from the atmosphere. Lundegärdh observed that during the day the carbon dioxide content of the air is considerably lowered. At night the 'respiration' of the soil once more restores the balance. This balancing of carbon dioxide without profit or loss takes place only on soils of medium fertility. On poor ground, plants absorb more CO_2 than is lost by the soil, hence with the growth of the plants, the soil becomes enriched in humus. On the contrary, in soils very rich in humus the loss of CO_2 may exceed the accumulation of organic compounds by the plants. An especially great abundance of CO_2 has been found in forests under the cover of trees where in the lower layers of air, CO_2 may reach a concentration of 0·08%, instead of the average 0·03%. This high percentage of CO_2 compensates the shade plants to a certain degree for the lack of light."[2]

Influence of Intermittent Light.

Warburg (1919) working with *Chlorella* and intermittent light reported that in strong light the velocity of photosynthesis is greater than in continuous light of the same intensity acting for equal periods of illumination. The more quick the change of light and dark periods, the greater the velocity of photosynthesis. When the light is altered 8000 times per minute, the photosynthetic velocity is 100% higher than that in continuous light and photosynthesis is only 10% higher than in steady light when there are only four alterations per minute. When the light intensity is feeble, alterations of light and dark periods do not influence the velocity of photosynthesis;

Warburg explains this peculiar behaviour from the view point of the existence of a reaction taking place in the dark to a position of equilibrium but constituting one of the stages in carbon assimilation. The explanation of Warburg seems unsatisfactory. A better explanation is offered by the writer in the following pages.

Sir J. C. Bose (1924) carried on experiments on *Hydrilla* with intermittent light, the source being sunlight or point-o-lite lamp and observed with point-o-lite lamp, an enhancement of 21% in carbon assimilation with an intermission of 1 second; with intermission of 2 seconds, an increase of 8% was obtained. With sunlight also, a slight enhancement in photosynthesis was observed with an intermission for 0·5 seconds. When the periods of intermission are increased, the velocity of photosynthesis decreases to a minimum and then increases again.

In photochemical reactions, it has been frequently observed that a reaction started by light continues in the dark even if the light is cut off. This phenomenon of "after-effect" is of common occurrence in photochemical reactions and Dhar and collaborators (1926) have shown that this phenomenon is more pronounced when the light intensity is great and the reaction is highly sensitive to light. They have advanced the view that the life-period of the activated molecules produced by light absorption is considerably prolonged and that the slow reversion of the activated molecules into the inactive state is the main cause of the phenomenon of after-effect in photochemical reactions. Hence the enhancement of photosynthesis in intermittent light observed by Warburg and Bose appears to be a case of "after-effect" of the photochemical process involved in carbon assimilation. The photosynthesis started by strong light persists even in the dark and hence the amount of photysynthesis appears to be greater in intermittent light than in continuous light. It is interesting to note that plants grown in artificial light develop much better when irradiated continuously during day and night than when subjected to a period of darkness for 8-12 hours. It appears, that night's rest is not necessary for plants. The possibility of work without rest for several months seems wonderful.

Some Products of Photosynthesis.

It appears that the hexoses are the first products of photosynthesis. The assimilation of carbon dioxide takes place in definite parts of the cell in the green plastids. Non-green plastids, such as the

colourless leucoplasts and the yellow and orange chromoplasts (existing in fruits and petals of flower) cannot accomplish photosynthesis. The leucoplasts can convert sugar into starch as in potato tubers and other underground storage organs and this is in agreement with the view that the conversion of sugars into starch is a secondary reaction and not directly associated with photosynthesis.

There is difference of opinion regarding the first substance formed in photosynthesis. It is generally believed that the simpler hexoses, glucose and fructose are likely to be formed before the complex disaccharides are obtained in carbon assimilation, although several investigators, notably Brown and Morris (1893) concluded that sucrose must be the first sugar, which is formed in photosynthesis, because sucrose appears to be in excess of glucose and fructose in the plant leaf. The excess of sucrose was supposed to be converted into starch, whilst for translocation, sucrose was transformed into glucose and fructose.

It is well known that in the animal body the following equilibrium exists:

$$\text{Glycogen} \rightleftharpoons \text{Glucose} \rightleftharpoons \text{Lactose}$$

Parkin (1925) has pointed out that sucrose is a product special to to the vegetable world, and he suggested tnat very likely the following equilibrium exists in the plant:

$$\text{Starch} \rightleftharpoons \text{Glucose} \rightleftharpoons \text{Sucrose}$$

Chapman (1926), however, believes that the following direct and reverse changes occur:

1. $\text{Glucose} \xrightarrow{\text{maltase}} \text{Maltose} \xrightarrow{\text{diastase}} \text{Starch.}$

2. $\text{Starch} \xrightarrow{\text{diastase}} \text{Maltose} \xrightarrow{\text{maltase}} \text{Glucose.}$

Saposchnikoff (1890) reported that only 64-87% of carbon dioxide absorbed in the plant leaf appears in the form of carbohydrates. If this observation of Saposchnikoff be correct, it appears that other products are simultaneously formed along with carbohydrates in photosynthesis. If the carbohydrate formed in photosynthesis is a hexose then from 1 g. of carbon dioxide absorbed 0·68 g. of the carbohydrate will be formed. If starch is formed then 0·613 g. is

expected from 1 g. of carbon dioxide and in case of sucrose, 0·647 g. is to be formed.

Krascheninnikoff (1901) concluded that besides carbohydrates other substances are formed in photosynthesis.

Sir J. C. Bose (1924) from his experiments with *Hydrilla* obtained the value 0·8906 for the theoretical ratio,

$$\text{Glucose}/\text{Oxygen} = 180/192 = 0{\cdot}9406.$$

It appears from these results that carbohydrates are not the only products of photosynthesis but along with them fats and proteins are likely to be synthesised. Meyer (1917) advanced the view that oil drops, which appear in the chloroplasts of *Vauchero* are directly formed by photosynthesis.

Moreover, several authors have reported that small amounts of hydrogen peroxide can be detected in photosynthesis. It may be possible that the hydrogen peroxide detected in leaves is a product of respiration. Looking at the whole problem from a broad point of view, it appears that formaldehyde, which is the first product of photosynthesis, polymerises to hexoses, which in their turn, are converted into sucrose. This carbohydrate in presence of light becomes inverted into a mixture of fructose and glucose as has been observed by Dhar and co-workers (1921). Hence there appears to be an equilibrium between the amounts of sucrose and hexoses in plants. In the subsequent pages it will be shown that proteins are likely to be formed in nature by the interaction of formaldehyde and carbohydrates and nitrates or nitrites present in plants. Hence along with the carbohydrates, proteins are formed by photosynthesis in plants. But the chief product of photosynthesis is certainly carbohydrate, and the hexoses formed from the polymerisation of formaldehyde appear to be the first products in carbon assimilation.

Baeyer Theory of Formaldehyde Formation in Photosynthesis.

Most of the theories on the mechanism of photosynthesis in plants postulate the formation of formaldehyde from carbon dioxide and water in presence of light and the polymerisation of formaldehyde to reducing sugars. It is assumed that in the first stage, considerable amount of energy is absorbed but in the second stage, not much energy absorption is necessary.

The originator of the hypothesis regarding the formation of formaldehyde as the first stage in photosynthesis and its condensation to

reducing sugars was the great organic chemist Adolf Baeyer. His theory rests mainly on the observation of Butlerow (1861) that trioxymethylene, which is a condensation product of formaldehyde, forms a syrupy substance behaving like sugar when heated with an alkali. Baeyer's theory published in 1870, may be briefly summarised as follows:

Bayer assumed that under the influence of light, the carbon dioxide absorbed by chlorophyll, undergoes decomposition into oxygen and carbon monoxide, which is fixed up by the chlorophyll and oxygen escapes. The carbon monoxide is assumed to react with hydrogen and forms formaldehyde, which in its turn polymerises to glucose as was first observed by Butlerow in 1861. He observed the formation of sugars from formaldehyde in presence of alkali. Baeyer assumed the formation of sugar from formaldehyde under the influence of the cell contents and possibly of alkalis. Baeyer is silent regarding the origin of the hydrogen necessary for the formation of formaldehyde from carbon monoxide. Several authors after Baeyer have assumed that water is decomposed into hydrogen and oxygen, the hydrogen being taken up in the formation of formaldehyde and the oxygen is set free. It is well known that in ultraviolet light water is decomposed into hydrogen and oxygen but no evidence is available whether in the plant, this decomposition takes place in presence of those radiations which lead to photosynthesis in the green plant. Some authors, however, ascribed the production of hydrogen to causes other than the decomposition of water.

Baeyer's theory received considerable support in view of the observation, that the ratio of CO_2 absorbed and O_2 given out is unity and this relation is satisfied if we assume that formaldehyde is the first product formed in photosynthesis.

Detection of Formaldehyde in Plants.

Several authors notably Reinke (1881), Curtius (1897), Pollacci (1900-1907), Grafe (1906), Kimflin (1907), Gibson (1908), Chodat and Schweizer (1915) and others reported the formation of formaldehyde in green leaves after illumination. On the other hand, Maze (1920) Rouge (1921), and Sabalitschka and Riesenberg (1924) could not detect any formaldehyde in plant tissues. Moreover, Spoehr (1913), and Fincke (1913), reported that in presence of light various organic substances present in the plant tissue decompose in light with the formation of formaldehyde. It appears from the foregoing observa-

tions that the formaldehyde in the assimilating plant tissues has not been proved beyond doubt. Recently Klein and Werner (1926) conclude from their experiments that formaldehyde and acetaldehyde occur in green leaves. Only formaldehyde was detected in leaves in which photosynthesis has occurred. It was not present in leaves kept in an atmosphere free from carbon dioxide or grown in darkness and in leaves poisoned by phenylurethane or hydrocyanic acid. On the other hand, acetaldehyde was detected in the leaves kept in the dark or those poisoned. Barton-Wright and Pratt (1930), however, have reported that formaldehyde is not a product of photosynthesis in plants but is generated by the action of light on bicarbonates and carbonic acid present in the outside water.

Experiments on Feeding with Formaldehyde.

If formaldehyde was an intermediate product of photosynthesis plants should be able to absorb this product from an atmosphere containing this substance and grow without the presence of carbonic acid. Numerous experiments have been carried on this line, and there is a general agreement amongst workers on this problem that formaldehyde in low concentrations can act as a plant food. Thus Loew (1899) and Bokorny (1888-1911) reported that in absence of carbon dioxide, but in presence of the formaldehyde-sodium bisulphite compound, *Spirogyra* can produce starch. Similarly Boitreux (1920), Moore and Webster (1920) and others reported the utilisation of formaldehyde by different plants. Grafe and Viser (1911), and Miss Baker (1913) could utilise gaseous formaldehyde as plant food in light, whilst the same result was obtained by Jacobi (1919-29) and Sabalitschka and Reisenberg (1924) in the dark, with several plants. Moreover, Bodnar, Roth and Bernauer (1927) observed an increase in the dry weight and the amount of carbohydrate in leaves exposed to formaldehyde vapour. According to Sir J. C. Bose (1924) formaldehyde, in small doses, serves as stimulant to the growth of plants.

Reduction of Carbonic Acid and Formation of Formaldehyde in vitro *from Carbonic Acid and Bicarbonates.*

From the chemical point of view, the main reaction involved in the first stage of photosynthesis seems to be the reduction of carbonic acid to formaldehyde.

$$H_2CO_3 \rightarrow H_2CO + O_2$$

Hence, to imitate the main chemical change involved in photosynthesis numerous chemists have attempted to reduce carbonic acid and bicarbonate solutions *in vitro* by different reducing agents. Thus Lieben (1895) and Ballo (1884) reduced carbonic acid to formic acid by the action of sodium and other amalgams, whilst Moissan (1902) obtained potassium formate by the reduction of carbonic acid by the action of potassium hydride. Fenton (1907) by the action of metallic magnesium on carbonic acid obtained formate as the chief product with traces of formaldehyde. On the other hand, Dhar and Atma Ram (1932) obtained considerable amounts of formaldehyde by the reduction of potassium bicarbonate solutions by powdered metallic magnesium without any trace of formate. This reaction also takes place with carbonic acid instead of bicarbonate. In place of metallic magnesium, cerium, tungsten and iron with carbonic acid have been used with similar results. This reduction of carbonic acid to formaldehyde is accelerated by sunlight. The importance of this research lies in the fact that carbonic acid and bicarbonates are directly converted into formaldehyde, which appears to be also the chief product in the first stage of carbon assimilation and that the reaction is accelerated by light.

Bredig and Carter (1914) obtained formic acid by the reduction of carbon dioxide by hydrogen under pressure in presence of palladium used as a catalyst and some carbonates. Schaper (1910) reduced carbon dioxide under pressure by ferrous oxalate.

By the action of silent electric discharge on mixtures of carbon dioxide and water, formic acid and formaldehyde were detected along with other products. Fischer and Priziza (1914) obtained formic acid and traces of methyl alcohol by the electrolytic reduction of carbon dioxide under 10-15 atmospheric pressures. Coehn and collaborators (1910) observed that dry carbon dioxide is decomposed by extreme ultraviolet light and Berthelot and Gaudechon (1910) reported that when hydrogen and carbon dioxide are exposed to light, formaldehyde and its condensation products are formed.

Reduction of carbonic acid in presence of different catalysts has also been effected in presence of light. Thus Usher and Priestley (1911) and Moore and Webster (1913) obtained traces of formaldehyde by exposing carbonic acid and water in presence of ferric and uranium salts, colloidal ferric hydroxide and some dyes, to ultraviolet and visible light. Stoklasa and Zdobnicky (1911-1913) obtained formaldehyde when carbon dioxide and hydrogen with potassium hydroxide were exposed to ultraviolet light. Dhar and Sanyal (1925) obtained

formaldehyde by exposing carbon dioxide to tropical sunlight when it is passed in beakers containing conductivity water. The formation of formaldehyde is facilitated by the presence of methyl orange, methylene blue, ferric chloride, uranyl salt, chromium salt, colloidal ferric hydroxide, chlorophyll, etc. Gopala Rao and Dhar (1931), and Atma Ram and Dhar (1932) obtained formaldehyde by passing carbon dioxide into solutions and suspensions of different substances in water when exposed to tropical sunlight. Nickel carbonate, manganous chloride, and cobalt carbonate produce good results. Methylene blue and malachite green act as good photosensitisers in the formation of formaldehyde from carbon dioxide and water exposed to tropical sunlight. It is interesting to note that in presence of several fluorescent substances like rhodamine, fluorescein, cartharamine, safranine practically no formaldehyde was synthesised photochemically from carbon dioxide and water, although the fluorescent substances were decolourised in presence of sunlight. Moreover, formaldehyde has also been obtained by exposing solutions of alkali bicarbonates with different photosensitisers. With nascent carbon dioxide obtained by the interaction of hydrochloric acid and carbonate no coloured photosensitisers seem to be necessary for the formation of formaldehyde in tropical sunlight. In all these cases the yield of formaldehyde was much greater than the limit of sensitiveness of the tests employed. In view of this fact and the careful blank experiments always carried on side by side, there is hardly any doubt that formaldehyde is actually obtained from carbon dioxide and water in tropical sunlight. Moreover, by exposing solutions of potassium bicarbonate alone and with freshly prepared carbonates of zinc, magnesium and iron (ferrous) in sealed glass bulbs appreciable amounts of formaldehyde were obtained.

These researches of Dhar and collaborators have been confirmed by similar observations of Mezzadroli and his colleagues. Thus Mezzadroli and Gardano (1927) have obtained formaldehyde and small amounts of sugar, by exposing solutions of bicarbonates of different metals to ultraviolet light. Ammonium bicarbonate produces a better yield of formaldehyde than the alkali bicarbonates, but the greatest yield of formaldehyde is obtained from calcium bicarbonate. The amount of formaldehyde generated rises to a maximum and then gradually decreases owing to its oxidation and polymerisation. Moreover, Mezzadroli and Vareton (1928) have shown that exposure of these bicarbonate solutions and carbonic

acid to ultraviolet rays causes an increase in the reducing powers of the solution to a maximum followed by a rapid fall. The presence of colloidal or reducing catalysts increases the reducing powers. Mezzadroli and Vareton have also reported that the yield of formaldehyde and sugars is increased by the addition of metallic magnesium to the calcium bicarbonate solution. Mezzadroli and Babes (1929) have stated that the reducing power of a 5% solution of potassium bicarbonate exposed to ultraviolet light increases to a constant value in presence of an active variety of carbon. When zinc is present with the carbon the reducing power is still further increased.

Recent experiments carried on in these laboratories with great care along with blank experiments, show that formaldehyde is synthesised and detected when dilute solutions (5 %) of bicarbonates of the alkali metals are exposed to sunlight for about 4 hours in thin layers (0·5 cm. thick) either in open dishes (11 cm. diameter) or in dishes covered with silica plates at temperatures upto 30°, higher temperatures are prejudicial to formaldehyde production. The amount of formaldehyde photosynthesised per 100 c.c. of solution exposed is 0·00007 – 0·0001 g. Schryver's reagent is most sensitive for the detection of formaldehyde in small quantities. The amount of formaldehyde obtained from exposing the bicarbonate solutions in the same dishes placed in a bath at 40° is about one third of that obtained at 30° under identical conditions.

It will be of interest to note that in nature the amount of carbon assimilation is less at 40° than at 30° as will be evident from the following observations.

Miss G. L. C. Matthaei (1905) observed that the amounts of CO_2 assimilated by a cherry laurel leaf per 30 sq. cm. (about 8 sq. inches) per hour at various temperatures were:

Temp.	6°	8·8°	11·4°	15°	28·7°	30·5°	37·5°	40·5°	48°
Wt. of CO_2 assimilated (g)	·0002	·0038	·0048	·0101	·0070	·0157	·0238	·0149	·0102

But the total dry weight of organic matter produced during the whole life of the plant may not increase with temperature in this way. Bialoblocki's (1871) results with barley are as follows:

Temperature	0°	10°	20°	30°	40°
Dry matter formed (g.) ...	Nil	7·64	8·22	3·85	0·93

Similar results have also been obtained by Baly and collaborators *in vitro*.

In tropical countries, the optimum temperature of photosynthesis in plants, as a rule, seems to be higher than with plants growing in temperate climates.

Since 1870 when Baeyer gave out his formaldehyde hypothesis, numerous attempts have been made to obtain formaldehyde *in vitro* from carbon dioxide and water on exposure to light. Usher and Priestley (1911), Baly, Heilbron and Barker (1921), Dhar and co-workers (1925-32), Mezzadroli and collaborators (1927-29), Yoe and Wingard (*J. Chem. Phys.*, 1933, **1**, 886) and others obtained positive evidence of formaldehyde formation from carbonic acid or bicarbonates in presence of catalysts, when exposed to light. On the other hand, Spoehr (1923), Baur and Rebmann (1922), Porter and Ramsperger (1925), Bell (1931), Emerson (1929), Zschiele (1932), Mackinney (1932), and Qureshi and Mohammad (1932) obtained negative results, although Mackinney made the following significant statement

" The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro*."

Baly and co-workers (1927) seem to contradict their earlier results.

Formaldehyde in Rain Water and in Upper Atmosphere.

Recently a new aspect of the problem has been brought forward by the observations of Dhar and Atma Ram (1932), that freshly collected rain water always contains appreciable amounts of formaldehyde. It is believed that formaldehyde in rain water is formed by the combination of carbon dioxide and water vapour present in the atmosphere by the absorption of ultraviolet light from the sun.

We have continued our analysis of rain water for formaldehyde and we have observed that all samples of rain water contain formaldehyde varying from 0·00015 to 0·0012 g. per litre. It is interesting to note that the amount of formaldehyde per litre of rain water obtained after some sunny days is practically the same as photosynthesised by exposing solutions of potassium bicarbonate to sunlight. It may be that the amount of formaldehyde in both cases is controlled by the equilibrium,

$$HCHO \rightleftharpoons H_2 + CO.$$

We have shown that the incidence of lightning discharge and thunderstorm does not increase the amount of formaldehyde present

in rain water. On the other hand, we have observed that the amount of formaldehyde present in rain water is greater when the rainfall is preceeded by some clear sunny days. Hence we are inclined to the view that formaldehyde in rain water is obtained as a result of its photoformation from carbon dioxide and water in the atmosphere.

It is well known that the following reaction requires ultraviolet of wavelength 2550Å.

$$CO_2 + H_2O + 112{,}000 \text{ cal} = H{\cdot}CHO + O_2$$

It is apparent that very seldom all the active rays are absorbed by a medium and hence it seems that all short ultraviolet rays coming from the sun will not be absorbed by the ozone layer present in the atmosphere. Some of the short wave radiations are likely to pass through the ozone layer and decompose water into H and OH, and these hydrogen atoms may reduce CO_2 to formaldehyde as has been observed by Bonhoeffer (1927) and P. Harteck (1933). This reduction of carbon dioxide by atomic hydrogen may be accelerated by the solar radiations. The heat of dissociation of water into H and OH is 110,000 calories. In other words, the energy required in the formation of formaldehyde from carbon dioxide and water is practically the same as that required in the breaking of H—OH link, which appears to be the first step in this process.

As the wave-length necessary for the formation of ozone (2020Å) is shorter than those necessary for the formation of formaldehyde (2550Å), it is expected that formaldehyde may be formed in the atmosphere at a height less than that of ozone.

Henri and Schou (1928) and Herzberg (1931) have shown that the ultraviolet absorption spectrum of formaldehyde vapour consists of 35 to 40 bands between 2500 to 3700Å with a maximum at 2935Å characteristic of aldehydes. The predissociation limit of formaldehyde appears to lie between 2680 to 2660Å with diffuse bands. On irradiating formaldehyde vapour with rays of wave-length between 2800 and 2650Å, Kirkbride and Norrish (1931) obtained a quantitative decomposition of formaldehyde into CO and H_2.

It is apparent, therefore, that not only ozone but also formaldehyde present in the atmosphere absorbs short rays from the sun. Hence the absorption of solar radiations shorter than 2900Å, which has been so far attributed to the presence of ozone, may be partially due to the formaldehyde present in the atmosphere.

Just as there is an equilibrium in the atmosphere between the oxygen and the ozone, it is evident, that the following equilibrium may exist in the atmosphere.

$$HCHO \rightleftharpoons CO + H_2$$

It is well known that the upper atmosphere is rich in hydrogen. Consequently due to the presence of hydrogen, the photo-decomposition of formaldehyde will be markedly hindered and appreciable amounts of formaldehyde may exist in the atmosphere.

From the foregoing lines it will be seen that the wave-lengths of radiations suitable for formaldehyde formation (2550Å) and decomposition (2660A) are much nearer each other than in the formation (2020Å) and decomposition (2655Å) of ozone. Hence, there is greater likelihood of the decomposition of the formaldehyde as soon as it is synthesised than in the case of ozone, but due to the presence of hydrogen, appreciable amount of formaldehyde is likely to exist in the atmosphere.

Just as ozone can exist in the atmosphere at a height of a few kilometers above the earth's surface (compare Götz, Dobson and Meetham, *Nature*, 1933, **132**, 281), formaldehyde can also exist at similar heights and that is why it can be washed down by rain water, which has been found to contain formaldehyde. We have made many careful experiments to see whether air on the surface of the earth contains appreciable amounts of formaldehyde. Large volumes of air were aspirated slowly through 20 c.c. of distilled water contained in a glass tube from 6-24 hours, but no trace of formaldehyde could be detected in the water by applying the Schryver's test, showing thereby that although formaldehyde exists in the upper atmosphere, it does not occur in the atmosphere near the surface of the earth.

Formation of Sugars from Formaldehyde.

Thanks to the researches of several chemists, the problem of the formation of reducing sugars by the condensation of formaldehyde is on a better footing than that of the photosynthesis of formaldehyde from carbon dioxide and water vapour. Butlerow (1861), Loew (1886-1889), Fischer (1892-1905), von Euler (1906), Nef (1914), Spoehr (1926) and others have shown that under various conditions, specially in presence of alkalis, formaldehyde is converted into reducing sugars in the absence of light.

Spoehr obtained traces of sugar by exposing 3% solutions of formaldehyde with zinc carbonate or potassium nitrate to sunlight With lead and calcium hydroxides, which form sugars in the dark also from formaldehyde, the yield in light was greater. Inghilleri (1912) obtained sorbose by exposing formaldehyde and oxalic acid to light, whist Pribram and Franke (1912) prepared glycollic aldehyde by exposing formaldehyde to ultraviolet light in quartz vessels.

Baly and collaborators (1924-1931) have carried on important researches on the conversion of formaldehyde to reducing sugars in presence of ultraviolet light. Baly (1924) reported that "with an initial concentration of 40% formaldehyde, the maximum reducing power is 8% calculated as glucose and with 20 litres of formaldehyde, this can often be reached after 14 days of continuous illumination." Recently Baly and collaborators (1927) have denied the formation of formaldehyde from carbon dioxide and water in ultraviolet light as reported in their previous work, but have obtained glycol, glycerol and reducing sugars from exposing formaldehyde to ultraviolet light. They have shown that when a 40% formalin solution containing an excess of calcium carbonate is placed in a tank kept at 30° and exposed to ultraviolet light from four quartz mercury vapour lamps for a month and the mixture is stirred, 80% calcium formate, 5·6% of calcium glycollate, and 15% of a mixture containing glycol, glycerol, pentaerythritol and some reducing sugars are obtained. According to these authors, the action of ultraviolet light is represented by the following scheme:

$$H_2CO_3 \xrightarrow{\text{light}} H_2CO_3 \text{ (activated)} \longrightarrow H{\cdot}CHO + O_2$$

$$nH{\cdot}CHO \longrightarrow \text{carbohydrate.}$$

$$\text{Carbohydrate} \xrightarrow{\text{light}} \text{formaldehyde } (H{\cdot}CHO).$$

It is believed that the following stationary state is established by the action of ultraviolet light on carbonic acid:

$$6\, H_2CO_3 \rightleftharpoons C_6H_{12}O_6 + 6\, O_2$$

When the concentration of carbohydrate is small and in presence of reducing agents, the reaction would proceed from left to right with the formation of carbohydrates, which would be photochemically decomposed to formaldehyde. Moreover, Baly and co-workers (1931)

observed that when various sparingly soluble substances, capable of absorbing carbon dioxide are used and carbon dioxide was passed and the whole was exposed to ultraviolet light, complex organic compounds containing carbohydrates, which char readily and develop reducing power after hydrolysis with hydrochloric acid, are formed. Among the powders which behaved in this way were metallic aluminium, barium sulphate, freshly precipitated aluminium hydroxide, basic carbonates of magnesium and zinc, ferric, chromic, and alumiuinm hydroxides with small amounts of thorium hydroxide deposited on kieselguhr, etc. They also used coloured substances like nickel or cobalt carbonates alone or deposited on kieselguhr with small amount of thorium carbonates in aqueous carbonic acid and visible light. The organic substances formed reduced Benedict's solution, gave the Rubner and Molisch reactions and formed a solid osazone. Under comparable conditions the use of visible light and coloured surfaces gave a greater yield of organic matter with a higher carbohydrate content than the use of ultraviolet light and white surfaces. It appears that the exclusion of ultraviolet light prevents the photo-decomposition of the carbohydrates formed. When a solution of ammonium carbonate containing a suspension of nickel or cobalt carbonate is exposed to visible light, complex nitrogenous organic compounds are formed.

Baly and collaborators have pointed out that the thermochemical equation,

$$6\ H_2CO_3 = C_6H_{12}O_6 + 6O_2 - 678800 \text{ calories}$$

requires the wave-length 2552Å for the activation of carbonic acid by means of radiation alone. Since photosynthesis occurs in the plant with visible light, some other mode of activation must be discovered. These authors state " the total quantity of energy necessary for photosynthesis to take place is supplied in two separate amounts, one quantity being given when the adsorption on the surface takes place, and the second quantity being given out by light ". It should be pointed out that a similar behaviour is observable with several other photochemical reactions, which are sensitised by different substances.

Recently Baly and Hood (1929) have shown that if the yield of carbohydrates (weight of photosynthesised organic matter soluble in absolute methyl alcohol) obtained from the presence of specially purified suspension of nickel carbonate (50 g.) in 1000 c. c. of water, is plotted against the temperature, the relation is found to be

a linear one between 5° and 31° (maximum yield being 0·0783 g.) after which there is a rapid decrease of yield. The values of the temperature coefficient for a 10° rise are in good agreement with those observed by Warburg (1919) with the unicellular alga, *Chlorella* under constant illumination. Baly and Hood have pointed out the close analogy between the photosynthesis *in vitro* and *in vivo* with special reference to the researches of Miss Matthaei (1905) on the assimilation of carbon dioxide at various temperatures and to the fact that the process both in the living leaf and in the laboratory has an upper and a lower temperature limit.

Dhar and co-workers (1925-1932) have studied the conversion of formaldehyde solutions to reducing sugars in presence of catalysts in sunlight. Dhar and Sanyal (1925) and Atma Ram and Dhar (1932) obtained reducing sugars by exposing solutions of formaldehyde with ferric chloride to sunlight. When solutions of formaldehyde are exposed to sunlight for periods varying from 60 to 125 hours with catalysts like ferric chloride, zinc oxide, nickel carbonate, chlorophyll, methylene blue and methyl orange, reducing sugars are detected. The best results obtained so far are those with ferric chloride. It will be of interest to note that formaldehyde solutions when mixed with fluorescent substances like safranine, cartharamine, rhodamine, etc., and exposed to sunlight, do not form reducing sugars, whilst with chlorophyll, reducing sugars are produced. The sugars obtained reduced Benedict's solutions and gave the Molisch and Rubner reactions. On exposing 1% solution of formaldehyde in presence of freshly prepared dilute ferric chloride in thin layers in open dishes, reducing sugars can be obtained even after an exposure of 4 hours.

Influence of Temperature on Sugar Formation from Formaldehyde.

As the yield of reducing sugars on exposing formaldehyde solutions to sunlight was best with ferric chloride, it was thought profitable to determine the temperature coefficient of this polymerisation for a 10° rise of temperature. 800 C. c. of 3% formaldehyde solutions were exposed in a sealed bulb with enough ferric chloride to sunlight for 45 hours at 30° and 40°. After the removal of the ferric and ferrous salts formed by the reduction of the ferric chloride, the solutions were evaporated to complete dryness, and freed from formaldehyde. The dried mass was extracted with pure methyl alcohol. The residue obtained after removal of methyl alcohol was estimated

by the reduction of Fehling's solution. The amount of CuO obtained at 30° = 0·061 g. ≡ 0·1355 g. of glucose, whilst at 40° the CuO = 0·077 g. ≡ 0·16 g. of glucose. Hence the temperature coefficient for a 10° degree rise of temperature between 30° and 40° for the conversion of formaldehyde solutions to reducing sugars in presence of ferric chloride in sunlight is 1·2. In this connection, it will be of interest to note that van Amstel (1916) obtained the value 1·26 for 10° rise of temperature between 24° and 36·5° in photosynthesis with *Elodea* and Sir J. C, Bose obtained the value 1·22 for a 10° rise between 20° and 30° in photosynthesis with *Hydrilla*.

Photosynthesis of Nitrogenous Compounds.

From our experiments on exposing solutions of formaldehyde and nitrite or ammonia to sunlight, we observe that methylamine is fairly easily obtained. Hence, it appears that in the absence of carbohydrates the products of photosynthesis of nitrogenous compounds will essentially consist of substances like pyridine, piperidine, etc., formed by the reaction of methylamine and formaldehyde and these compounds have actually been obtained by several workers including ourselves. In presence of carbohydrates, however, we are likely to obtain alkaloids like nicotine, but especially amino-acids by the reaction of aldehydes of the monobasic and dibasic acids obtained from starch and carbohydrates with ammonia or methylamine. It appears, therefore, that in nature, also amino-acids, the precursors of proteins are formed by the reactions of ammonia or methylamine on the derivatives of carbohydrates and that is why the formation of proteins in plant goes hand in hand with the formation of carbohydrates, which require light. Several workers have reported that the formation of proteins in nature is facilitated by the presence of carbohydrates or light. Moreover, it appears that protein formation in plants is likely to be facilitated by the presence of fats, which yield glycerol readily. It has been shown by Dhar and collaborators that reducing sugars are obtained by exposing glycerol to sunlight. Recently we have observed that reducing sugars are obtained by exposing to air and light solutions of tartaric acid and other organic acids in presence and absence of photocatalysts. Hence the presence of tartaric acid or other hydroxy organic acids may also favour the formation of proteins in plants.

It is well known that in the animal body, proteins are converted into glucose. In the plant kingdom the formation of proteins is

facilitated by the presence of glucose. It appears, therefore, that in photosynthesis protein formation is likely to take place when some carbohydrates have already been formed.

Appreciable amounts of nicotine have been photosynthesised and the molecular weight of the base determined from the chloroplatinate of the base on exposing dilute solutions of ammonia, formaldehyde and cupric salts in presence of catalytic surfaces like ZnO, TiO_2, etc., to sunlight for about 80 hours. Moreover, when solutions of glycol and potassium nitrate are exposed to sunlight for about 8 hours in presence of TiO_2 as a photocatalyst, tests for glycine are obtained. Similarly a solution containing glucose and potassium nitrate with TiO_2 as a photocatalyst when exposed to sunlight for the same period, appears to produce arginine. Longer exposure causes the disapearance of the amino-acids photosynthesised, probably due to their photo-oxidation. Solutions of ammonium lactate form amino-acids when exposed to light. These amino-acids obtained in photosynthesis can be readily tested by the valuable "ninhydrin" test.

The mechanism of photosynthesis of proteins by the injection of potassium nitrate in the stem of *Helianthus annuus* has been studied by Varadachar (1932).

Influence of Temperature on Photosynthesis.

Many plant physiologists following the lead of Blackman have applied the van't Hoff rule to plant temperature studies. The application of the Arrhenius relation has been found to be general with ordinary chemical reactions. When the same relation is applied to the results actually obtained regarding the influence of temperature on photosynthesis in plants, it fails, as will be evident from the following table obtained from Warburg's results (1919).

Light intensity.	Observed $\frac{k_t+10}{k_t}$.	Calc. $\frac{k_t+10}{k_t}$.
16	2.0	4·11 between 16° and 25° (taking 4·7 between 5° and 10°).
45	2·0	4·01 between 10° and 20° (taking 4·3 between 5° and 10°).
45	1·6	3·66 between 20° and 30° (taking 4·8 between 5·4° and 10°).

These results have been calculated by applying the Arrhenius relation. It appears that the temperature coefficients of photosynthesis do not obey the Arrhenius relation, which has been found to be universally applicable to ordinary chemical reactions investigated so far and no case of failure has been reported. In photosynthesis, the observed values are always smaller than the calculated values. The reasons of the non-applicability of this relation to photosynthesis in plants are: (*i*) the greater influence of temperature on the respiration process than that on photosynthesis and, (*ii*) the harmful influence of high temperature on the chloroplast.

When the temperature of a plant system undergoing photosynthesis is increased the velocity of photosynthesis is increased but to a smaller extent than that of respiration. Consequently, the temperature coefficient of the observed photosynthesis will appear to be smaller than when the reversible reaction was not present. Moreover, the chloroplast in the protoplasmic cell which is likely to be active in the photosynthetic process starts undergoing deterioration when the temperature is greater than 20° and may be partially destroyed when the temperature is still greater. This is evident on comparing the results obtained by Warburg and those calculated from the Arrhenius relation. The observed temperature coefficients between 16° and 25° and between 10° and 20° are nearly half of the calculated values, whilst the observed temperature coefficient between 20° and 30° is much less than half of the calculated value. The pernicious influence of high temperature on physiological and enzymatic and bacterial processes is well known. In most cases the optimum temperature in these reactions is round about 20°. Moreover in plant photosynthesis, there is an additional factor namely, the reverse reaction, *e.g.*, respiration, which is also simultaneously going on and is counterbalancing the photosynthetic reaction and hence, the influence of temperature on photosynthesis is less pronounced due to these counteracting agencies.

It has been observed that in the case of some chemical reactions, the temperature coefficient can have the high value 7·2. Hence it is no wonder that the temperature coefficient of photosynthesis at low temperatures (say between 5° and 10°) has the value 4·3. It seems probable that the photosynthetic reaction is not an adsorption process of which the average temperature coefficient is in the neighbourhood of 1·2 for a ten degree rise of temperature, but it is controlled by a truly photochemical change having a moderately high

temperature coefficient. In several communications from our laboratories it has been shown that the photochemical reactions need not have temperature coefficients approaching unity, but can have values as high as 4. From the foregoing considerations, it is clear that it is needless to assume that the photosynthetic process involves two reactions. It is believed that in high light intensity the chemical reaction ("Blackman reaction" as designated by Warburg) is determining the total velocity of the reaction, because for a ten degree rise of temperature between 15° and 25°, the velocity of the photosynthesis is doubled. On the other hand, in low light intensity, the temperature coefficient instead of being 2 as with intense light, is 1·06 and hence it has been assumed that the chemical reaction is not the controlling factor as in the previous case; but the photochemical reaction with a low temperature coefficient determines the photosynthetic rate at low intensities of light.

In presence of intense light, the photochemical reaction causing the photosynthesis and having a moderately large temperature coefficient is predominant and the counteracting influence of the respiration process, which is not as much accelerated by light as the photosynthetic reaction, is not prominent. On the other hand, in presence of feeble illumination, the velocity of the photosynthetic reaction is not high, because this reaction takes place only in light and is proportional to the light intensity. In this case, the counteracting influence of respiration, especially at increased temperatures, becomes prominent and hence the influence of temperature on the observed photosynthetic rate is feeble.

Warburg (1919) has observed that the temperature coefficient of photosynthesis with the unicellular alga *Chlorella* is much less when the light intensity is feeble than when it is strong. Thus $kt+10/kt$ between 16° and 25° with light intensity sixteen $=2·0$ and $kt+10/kt$ between 15° and 25° with a relative intensity of one $=1·06$.

These results which appear to have been confirmed by other workers can be explained in the following way.

It has already been stated that in a plant, the following opposing reactions are taking place.

$$nCO_2+nH_2O \rightleftharpoons C_nH_{2n}O_n+nO_2$$

and the temperature coefficient of photosynthesis is less than that of respiration. Hence, when the light intensity is feeble, the velocity of photosynthesis is small and is slightly greater than that of respira-

tion at the same temperature. Now when the temperature of the system is raised through ten degrees, the velocity of the photosynthesis will be increased to a smaller extent than that of respiration. Consequently the temperature coefficient of the observed photosynthesis may be unity or less.

Moreover, in nature when the temperature of the air is high, the plants gain no material through photosynthesis because of the high respiration, whilst at lower temperature with the same light intensity, food materials are formed in the plant.

Willstätter and stoll (1918) have reported that leaves of low chlorophyll content exhibit a lower acceleration with increasing temperature than the leaves of high chlorophyll content. Thus leaves of *Ulmus* with low chlorophyll content showed a temperature coefficient of 1·34 and with high chlorophyll content of 1·58 between 15° and 25°. These results of Willstätter and Stoll can be explained from the view point already advanced.

The temperature coefficient (1·58) of the photosynthesis with chlorophyll-rich leaves is greater than that with chlorophyll-poor leaves (1·34), although the photosynthesis is not at all directly proportional to the amount of chlorophyll in the leaves. Willstätter and Stoll find that temperature variations do not affect the rate of photosynthesis of the yellow varieties as much as the normal ones. In the yellow varieties, the amount of photosynthesis being small, the compensating influence of respiration becomes prominent and hence temperature does not appear to influence photosynthesis with these varieties to the same extent as the normal ones with more chlorophyll.

Moreover, differences in light intensity have more profound effect on the yellow varieties than on the normal ones and the time factor appears more slowly than with the normal ones. It is well known that photosynthesis increases with the light intensity and the chlorophyll content of the leaves. Now in the case of leaves containing much chlorophyll, the velocity of photosynthesis will be high and may reach the maximum, even when the light intensity is not high and hence in these cases, the reaction will be less sensitive to the influence of light changes, because the reaction is already fast due to the presence of large amounts of chlorophyll. On the other hand, when the chlorophyll content is small, the reaction velocity is small and light will affect the velocity more markedly than in the previous case. This explanation is in agreement with the observations

of Willstätter [1] and Stoll that in the chlorophyll-rich leaves, an increase of light intensity was without influence on photosynthesis; in fact the light intensity could be reduced by $\frac{3}{8}$ without affecting the rate of photosynthesis. Exactly similar exhaustion effect has been observed with several photochemical reactions where the velocity of the reaction may be proportional to $I^{\frac{1}{3}}$ or $I^{\frac{1}{4}}$ in some cases where the reaction is very fast.

Even at low temperatures, photosynthesis goes on. Thus at $-6°$, photosynthesis was reported in leaves of cherry laurels by Miss Matthaei. In Alpine shade plants, photosynthesis is observed at $-16°$ and in lichens upto $-20°$. Jumelle (1891) reported the occurrence of photosynthesis at $-25°$, $-35°$, $-37°$ and even at $-40°$. Whilst with plants growing in warm, temperate, subtropical climates and water plants, photosynthesis stops between 0° and 2° and in tropical plants, it stops between 4° and 8°.

On the other hand, many plants resist high temperatures fairly well. Thus McGee (1921) reports that joints of a prickly pear attains a temperature of 55° without any visible harm. Wurmser and Jacquot (1923) have observed that several marine algae, when warmed upto temperatures varying from 36° to 45° for a period varying from 1–15 minutes show a smaller velocity of photosynthesis when brought back to their normal temperature (16°). The decrease of photosynthetic rate depends upon the temperature and the period for which the plants were subjected to the high temperatures.

The Phenomenon of "Solarisation".

It is well known that not only high temperature but also long exposure to strong light affects photosynthetic activity. Thus Ursprung (1917) observed that a leaf of *Phaseolus* after 5 hours of illumination showed very deep coloration of the starch-iodine, while after 8·5 hours' illumination, the reaction was faint. This phenomenon can be observed with almost any source of light of sufficient intensity and the time required is proportional to the light intensity. The effect is first brought about in the red-orange portion, the region showing the best photosynthetic activity. With higher intensity, the shorter wave-lengths bring about in shorter time and it is apparently proportional to the photosynthetic activity of light. Ursprung has called this phenomenon "solarisation" as it is analogous to the

phenomenon of solarisation observed in photographic plates under similar circumstances.

It is expected that not only with starch but with other carbohydrates, similar effect will be observed. This behaviour has been ascribed to the inactivation of chloroplasts. After long exposure to intense light, the plant organs are assumed not to function, although they are not killed and on keeping in the dark for a period, again produce starch normally.

The inhibiting effect of long exposure to light of high intensity on photosynthesis has long been studied by Ewart (1897) and the inhibiting effect has been ascribed to the destruction of chlorophyll. Pantanelli (1903) explains the fatigue effects observed by him in bright light from the viewpoints of chlorophyll destruction and injury to the chloroplast plasma. The observations of Ewart on *Allium cepa*, which does not form starch, indicate that when leaves of this plant are exposed to bright light for 14 days or for a shorter period while being fed with sugar, the evolution of oxygen finally ceases. This inactivation apparently does not injure the cells or chloroplasts. After a few days in darkness, the capacity for photosynthesis is regained.

The foregoing facts are explained from the following considerations.

In plants the following equilibrium exists:

$$nCO_2 + nH_2O \rightleftharpoons C_nH_{2n}O_n + nO_2$$

The direct action (photosynthesis) is being opposed by the reverse reaction (respiration), which will increase, according to the law of mass action with increase in the concentration of the carbohydrate, which is a product of photosynthesis. Consequently, with accumulation of carbohydrates or when the plants are fed with sugar, as was done by Ewart, photosynthesis is retarded and may stop altogether when the carbohydrate content becomes very high. When the illumination is high and it lasts for a long time, the carbohydrate content increases and along with it the respiration also increases, and thus the photosynthetic velocity falls off with time even when the illumination is continued. After a time, the respiration will more than counterbalance photosynthesis and the carbohydrates formed by the photosynthesis will be oxidised to carbon dioxide and water and will disappear on prolonged exposure. When the carbohydrates disappear the photosynthesis will again

begin. It has been known for a long time that the photosynthetic rate decreases with accumulation of the products of photosynthesis. Moreover, Saposchnikoff (1898) has demonstrated the inhibitory power of an accumulation of carbohydrates and that these cannot increase beyond a certain point. When the leaves of *Vitis vinifera* contain 23 to 29 % carbohydrates of dry weight, photosynthesis ceases and respiration predominates. Saposchnikoff has shown that as carbohydrates accumulate, decrease of photosynthetic rate takes place, whilst a decrease in the carbohydrate content results in an increased photosynthesis. These results are evident from the viewpoint of the reversible reactions already put forward.

Moreover, there are two other factors, which increase respiration, should be considered, *viz.*, (*i*) influence of light intensity on the respiratory process, and (*ii*) influence of increased temperature caused by prolonged light absorption.

Compensation Point.

The compensation point, *i.e.*, the light intensity at which the photosynthetic and respiratory activities of the plant compensate each other, decreases with decrease of temperature as will be evident from the following table.

Plant.	Intensity at 20°.	Intensity at 5°.
Spirogyra	174	26·7
Fontinalis	150	40
Cladophora	253·3	62·9
Cinclidotus	400	75

The foregoing results show that the light intensity which at 20° represented the compensation point produced an evolution of oxygen due to photosynthesis at 5°.

With *Cladophora*, with increasing temperature, the compensation point rises more rapidly than the rate of respiration determined in the dark; an increase of temperature from 5° to 25° causes the respiration to become 4·8 times greater in the dark, whilst the light intensity increases to 6·69 times.

The foregoing results as well as other facts regarding the compensation point can be explained from the following considerations:

1. Photosynthesis is proportional to the light intensity, there being no photosynthesis in the dark.

2. Respiration takes place in the dark but is appreciably accelerated by light.

3. An increase of temperature affects respiration more markedly than photosynthesis.

The fact that the compensation point rises with increase of temperature is due to the greater increase of respiratory activity than photosynthetic activity with increased temperature. The respiratory activity of the plant, which counterbalances the photosynthetic process, increases much more than photosynthesis at higher temperatures and consequently, the light intensity must be increased to cause more photosynthesis to counteract the increased respiratory activity. There is another reason for further increase in the respiratory activity of the plant. Hitherto, it has been assumed by most of the plant physiologists that the process of respiration is not accelerated by light. But it is evident from the researches of Dhar and collaborators (*vide*, "New Conception on Biochemistry") that animal metabolism is markedly accelerated hy light absorption. Hence, it seems pretty certain that the respiratory process taking place in plants is also accelerated by light. Consequently the respiratory activity of the plant is accelerated by two agencies, *e.g.*, temperature and light intensity and thus the light intensity required for increased photosynthesis in order to counteract this high respiratory activity should be very high. Thus with increasing temperature, the compensation point should rise more rapidly than the rate of respiration because of its additional enhancement by light absorption and this is clearly borne out from the experiments on *Cladophora* in which an increase of temperature form 5° to 25° causes the respiration to become 4·8 times greater when determined in the dark, whilst the light intensity increasee 6·69 times, for the compensation point.

It is evident that under certain circumstances, when the temperature is high and the light is intense, the compensation point may not be attained even with intense light and the plant will evolve carbon dioxide like an animal even in presence of light. This is likely to happen frequently in tropical countries where at the sea level, the heat rays of the sun become very prominent and the temperature of the plant will be high and photosynthesis cannot counterbalance respiration under these circumstances. At higher altitudes, the light rays are more active than at the sea level and it is expected that at these altitudes, very seldom, respiration will exceed photosynthesis in sunlight.

These conclusions are corrborated from the experimental results of Hardar (1921) with sea plants in the polar zones where the light intensity is not very high. Thus Hardar records the following ratio of photosynthesis and respiration for different temperatures were obtained.

20°-22°	0·588	0·4427	0·4280
2°-3·5°	1·603	0·9207	2·059

The position of the compensation point of a plant with reference to temperature is naturally of great importance to the life of the plants and its relation to the environment.

Formaldehyde in Dew and its Formation from the Photo-oxidation of Organic Compounds.

Dew has been found to contain appreciable amounts of formaldehyde. The quantity of formaldehyde is generally greater in dew than in rain water. The origin of the formaldehyde in dew seems to be the photo-oxidation of organic matter present on the surface of the soil. When solutions of organic substances like acetic acid, citric acid, glycine, malic acid, lactic acid, glycogen, acetone. etc., are exposed to sunlight and air, formaldehyde is readily formed. Dyes like malachite green, methyl violet, methylene blue, etc., also form formaldehyde readily on photo-oxidation. Tartaric acid, butyric acid, propionic acid and some dyes form smaller quantities, whilst oxalic acid, formic acid, glucose, cane sugar, starch, histidine, etc., produce very small amounts of formaldehyde from photo-oxidation.

It seems likely that the energy generated in the photo-oxidation of these organic substances supplies a part of the energy for the photo-formation of formaldehyde. We are of the opinion that in nature, the photosynthesis that is taking place in the plants is aided by the energy obtained in plant respiration, which goes on as long as the plant lives. The ease with which formaldehyde or other energy-rich compounds are formed in plants is partly due to their getting a constant supply of energy from the oxidation of the food materials present in the plant. We have postulated that the most important chemical change in the formation of carbohydrates in plants and in the formation of formaldehyde in nature from carbon dioxide and water is the photolysis of water into H and OH. The amount of energy required to decompose a gram

molecule of water into H and OH is approximately the same as that necessary for the formation of a gram of mole of formaldehyde from carbon dioxide and water. These are highly endothermal changes requiring radiations of wave-length 2550 Å (1,12,000 calories). In nature, however, photosynthesis takes place in visible light especially the red. We are of opinion that the energy derived from respiration in the plants already supplies a part of the energy necessary for the photosynthesis and thus rendering the photo-decomposition of water possible by longer wave-lengths. Although the adsorption of carbon dioxide and water by the chlorophyll of the leaf may partially activate these substances just as the adsorption of hydrogen and oxygen on a platinum or palladium surface renders them active, it appears to us that this activation of carbon dioxide and water by their adsorption on the leaf surface is less important than their activation by the absorption of energy from respiration.

There is an intimate relation between respiration and photosynthesis in the plant kingdom, because photosynthesis cannot proceed without the energy available from respiration for the partial activation of carbon dioxide and water vapour. The need of the presence of oxygen in photosynthesis is also explained from the same point of view.

It is easier to obtain from formaldehyde or any other energy rich compound from carbonic acid or bicarbonate solutions on exposure to light when a suitable exothermal reaction is taking place in the system along with the photosynthetic reaction.

A Theory of Carbon Assimilation.

The following appears to be the important steps in carbon assimilation.

(1) Partial activation of carbon dioxide and water at the leaf surface due to their adsorption by chlorophyll and other plant pigments. It seems that chlorophyll and carotinoids present in the leaf act as photosensitisers and as reducing agents in the photoreduction of carbonic acid. (2) Further activation of the adsorbed CO_2 and water by absorption of a part of the energy available from respiration and the oxidation of carotin and the formation of activated carbon dioxide and water as products of respiration. (3) Absorption of light by chlorophyll and other pigments and the

dissociation of activated water molecules in the leaf surface into H and OH and the reduction of activated carbon dioxide molecules to formaldehyde by the atomic hydrogen produced from the sensitised photolysis of water. The amount of energy required to decompose a gram mole of water into H and OH is the same as that necessary for the formation of a gram mole of formaldehyde from carbon dioxide and water. (4) The polymerisation of formaldehyde to reducing sugars. (5) The formation of hydrogen peroxide from OH and the rapid decomposition of H_2O_2 into water and oxygen on the leaf surface.

The polymerisation of formaldehyde *in vitro* to reducing sugars is an exceedingly slow process even in presence of light. We have shown that it is accelereted by ferric salts. Moreover, it is known that in presence of alkali, reducing sugars are formed from formaldehyde. Light accelerates this reaction. How the formaldehide formed on the leaf surface undergoes rapid polymerisation is still unknown. This theory of carbon assimilation appears to have more experimental evidence in its favour than those of Willstätter, Warburg, Wurmser and others.

It is interesting to note that the botanists are also realising the importance of chemistry in plant metabolism, as is evident from the following statement of R. W. Thatcher, an American botanist of repute:—" Hence we may say that the methods by which the plant machine (protoplasm) accomplishes its results are essentially and definitely chemical in character and may be studied purely from the standpoint of chemical reactions".

The Complex Formation between Cerium or Tungsten with Tartaric Acid in Alkaline Media.

By R. Raman and B. L. Vaishya.

Walden (*Ber.*, 1897, **30**, 2889) found that if uranyl salts are added to the active modifications of hydroxy acids, the optical rotation is changed and reaches a maximum, when the molecular proportions of the hydroxy compound to the salt is 1:1. This was afterwards studied by Grossmann and also by Darmois (*Comt. rend.*, 1923, **177**, 49) who also came to the same conclusion and attributed this change to a complex formation. The effect of antimony, boric and arsenic oxides, on the optical rotation of tartaric acid was studied by Grossmann (*Z. physikal. Chem.*, 1907, **57**, 533), that of the boric being recently re-investigated by Darmois (*Compt. rend.*, 1930, **190**, 371). The effect of tin on tartaric acid has been investigated by Dumaski and Kniga (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 220), that of hafnium and zirconium by Boer and Emmens (*Rec. trav. chim.*, 1930, **49**, 855), that of copper by Giuntini (*Compt. rend.*, 1930, **191**, 778), and that of molybdic acid in alkaline media by Darmois (*Trans. Faraday Soc.*, 1930, **26**, 384; *compt. rend.*, 1923, **176**, 1140). Recently the influence of thorium salts on the optical rotation of tartaric acid, and tartrates was undertaken by Darmois and Yen-ki-Heng (*compt. rend.*, 1932, **194**, 703). All these workers came to the conclusion that a complex formation takes place in such cases. Henderson and Prentice (*J. Chem. Soc.*, 1903, **83**, 260) have observed considerable change in rotation when molybdic and tungstic oxides are dissolved in lactic acid and potassium lactate.

In this paper an attempt has been made to study the effect of cerium and tungsten salts on the optical rotation of tartaric acid in alkaline media and to see if some complex formation takes place. The same result was also verified by another independent method, that of noting the change in p_H values of the substance by *e. m. f.* method, using hydrogen electrode.

Experimental.

Cerium Chloride and Sodium Tratrate.

Table I gives the results obtained with the polarimeter. It will be observed that the specific rotation goes on increasing with increasing amount of cerium chloride and reaches a maximum, when the solution contains 2 mols. of cerium chloride and 2 mols. of sodium tartrate. Following Henderson and Prentice (*loc. cit.*) $[\alpha]_D$ has been calculated from the formula

$$\frac{\alpha_D \times \text{vol. of solution}}{2\cdot[\text{wt. of Na-tatrate and wt. of } CeCl_3]}.$$

Table I.

Na-tartrate in 50. c. c.	$CeCl_3$ added.	Corresponding wt. of Ce_2O_3.	Molar prop. Na-tart : Ce_2O_3.	α_D^{25}.	$[\alpha]_D^{25}$.
0·26 g.	0	0	1 :0	+0·30	+28·85
,,	0·124 g.	0·055 g.	1 :0·25	+0·60	+47·6
,,	0·248	0·110	1 :0·50	+0·80	+54·1
0·39	0·496	0·219	1 :0·66	+1·80	+78·9
0·26	0·496	0·219	1 :1	+1·20	+62·9
0·26	0·620	0·278	1 :1·25	+1·20	+56·3

It was found that on diluting the solution there was no marked change in the specific rotation of the complex formed; but the temperature had an appreciable effect as is clear from Table II.

Table II.

Temp.	... 25°	40°	50°
α_D	... + 1·80	+ 1·90	+ 2·10
$[\alpha]_D$	... +78·9	+78·02	+86·3

Table III contains the results obtained by the *e. m. f.* method.

TABLE III.

Temperature = 18°.

Molar prop. of Na-tart : Ce_2O_3	... 1 : 0·0	1 : 0·25	1 : 0·50	1 : 0·66	1 : 0·75
p_H	... 11·10	11·61	12·89	12·48	12·68

It is remarkable to find that *e. m. f.* observations also show a rapid change in the p_H at the same place at which complex formation is observed with the polarimeter.

Cerium Nitrate and Sodium Tartrate.

TABLE IV.

Na-tartrate in 50 c.c.	$Ce(NO_3)_3$ added.	Corresponding wt. of Ce_2O_3.	Molar prop. Na-tart : Ce_2O_3.	α_D^{2}	$[\alpha]_D^{25}$
1·941 g.	0·0	0	1 :0	+2·35°	+30·3°
,,	0·661 g.	0·250 g.	1 :0·25	+2·70°	+30·8°
,,	1·322	0·500	1 :0·50	+3·95°	+40·1°
2·912	2·644	1·000	1 :0·66	+7·55°	+48·3°
1·941	1·983	0·750	1 :0·75	+5·10°	+47·4°

Effect of temperature on the optical rotation of the mixture at the compound formation is shown in Table V.

TABLE V.

Temp. ...	25°	40°	50°
α_D ...	+ 7·55°	+ 7·65°	+ 7·90°
$[\alpha]_D$ ...	+48· 8°	+48· 9°	+50· 5°

Table VI contains the results of *e. m. f.* measurements and p_H calculated.

TABLE VI.

Molar prop. Na-tart : Ce_2O_3	... 1 : 0	1 : 0·25	1 : 0·50	1 : 0·66	1 : 0·75	1 : 1·00
p_H	... 13·07	13·24	13·26	13·31	13·32	13·33

It will be seen that *e. m. f.* measurements also show the complex formation at those concentrations at which polarimetric investigations also indicate the formation of complexes. In order to see if sodium nitrate has a depressing effect on the complex formed, the ratio of the complex formation with sodium tartrate and cerium chloride was taken with excess of alkali, 20 c.c. of $M/15$- $NaNO_3$ were added and the solution was made up to 100 c.c., the specific rotation observed was the same as that with sodium tartrate and cerium nitrate. On the other hand if 20 c.c. of $M/15$- NaCl were added to the complex formation between sodium tartrate and cerium nitrate, there was no effect, the specific rotation being the same.

Sodium Tungstate and Sodium Tartrate.

TABLE VII.

Na-tartrate in 50 c.c.	Na-tungstate added.	Molar proportion Na-tartrate : Na-tungstate.	α_D^{20}.	$[\alpha]_D^{20}$.
0·3879 g.	0	1 : 0	+0·50°	31·4°
	0·1650 g.	1 : 0·25	+0·75°	33·2°
	0·3300	1 : 0·50	+1·00°	35·6°
	0·4950	1 : 0·75	+1·00°	28·1°
	0·6600	1 : 1·00	+1·00°	24·0°

TABLE VIII.

Effect of temperature at the compound formation.

Temp. ...	20°	40°	50°
α_D ...	+ 1·00°	+ 1·30°	+ 1·40°
$[\alpha]_D$ ...	+36·6°	+45·0°	+48·6°

TABLE IX.

Results obtained by e.m.f. measurements.

Molar prop. Na-tart : Na-tungstate ...	1 :0	1 :0·25	1 :0·50	1 :0·75	1 :1·00
p_H calc. (Temp. = 18°)	12·42	11·89	11·59	11·89	11·86

The complex formation in this case is indicated at the same place as that observed by the optical method above.

Potassium Tungstate and Potassium Tartrate.

TABLE X.

K-tartrate in 100 c.c.	K_2WO_4 added.	Molar prop. K-tart : K_2WO_4.	α_D^{20}.	$[\alpha]_D^{20}$.	Temperature 20° *e.m.f.* obs. (volts).	p_H calc.
0·4520 g.	0	1 :0	+0·20°	+22·36°	−0·4074 × 2·036	8·2
	0·1630 g.	1:0·25	+0·50°	+40·64°	−0·4266	8·9
	0·3260	1 :0·50	+0·95°	+61·05°	−0·5002	11·5
	0·4890	1 :0·75	+0·951°	+50·28°	−0·4990	11·4
	0·6520	0 :1·0	+0·95°	+42·06°	−0·4801	10·8

DISCUSSION.

Any compound formed by the interaction of the cerium or tungsten salt, with the normal alkali tartrate will be of the formula

$$\begin{array}{l}CHO\ (RO)\ COOM\\ |\\ CHO\ (RO)\ COOM\end{array}$$

where R represents the foreign substance and M, the sodium or potassium atom. This view is strongly held by Darmois (*Bull. Soc. chim. Belg.*, 1927, **36**, 64) who describes the formation of such compounds or complexes and says that those which are stable in excess of alkali, combine with the alcoholic hydroxy group of the acid, thus forming the compounds of the tartar emetic type (Henderson and Baar, *J. Chem. Soc.*, 1899, **75**, 542). It is observed from our work that when cerium nitrate or cerium chloride is added to an alkaline solution of tartaric acid, the optical rotation is increased and reaches a maximum, when the molecular proportions of cerium salt to tartrate is in the ratio of 2 : 3. It is probable that this change can only be due to the formation of new optically active compound or complex by the interaction of the inactive foreign substance and the active acid, the plausible formula of which appears to be on the basis of the views held by Darmois (*loc. cit.*) as $2Ce_2O_3 : (C_4H_4O_6M_2)_3$.

In the case of the tungsten salt the maximum rotation is obtained when the solution contains 1 mol. of the tungstic acid and 2 mols. of the tartrate, the complex formed will have a formula as WO_3 : $(C_4H_4O_6M_2)_2$.

When we examined the various solutions by an *e.m.f.* method and calculated the p_H values, we found that at the same point as

indicated optically, there is a complex formation denoted by means of a rapid change in the p_H. It is remarkable that at the point of complex formation in the case of cerium chloride, the p_H value is maximum, while in the case of the tungstic acid it occurs at the minimum.

By comparing the results of Tables I and IV, it will be found that the specific rotation observed in the case of cerium chloride and sodium tartrate at the complex formation is higher than that obtained for cerium nitrate and sodium tartrate. If in these two cases, the complex formed is the same, the same specific rotation should be expected. The presence of neutral salts like NaCl and $NaNO_3$, however, has some effect on the specific rotation of salts and esters of tartaric acid (Darmois, *Trans. Faraday Soc.*, 1930, **26**, 384; *Ann. physique*, 1928 **10**, 70). Darmois describes the negative effect of sodium chloride in the rotatory power of tartrate ion but has not investigated the effect due to sodium nitrate. Mallemann (*loc. cit.*) has described the effects of chlorides and nitrates of the alkali metals on the rotatory power of tartaric acid in aqueous solutions to be that of depression and is greater with the chlorides than with the nitrates. Our results obtained are in harmony with the views of Mallemann at least under the conditions of the experiment, using excess of the alkali.

Summary.

1. The complex formation between sodium tartrate and cerium salts was studied in alkaline media by means of a polarimeter and potentiometer and it was found that a complex formation thus takes place when the molar proportions of sodium tartrate and cerium salt is 3:2.

2. The complex formation between alkali tartrate and tungstates was also studied in alkaline media. The complex formation in this case is with two molecules of tartrate and one molecule of tungstic trioxide.

3. It was observed that the p_H value of cerium salt complex is at a maximum, where it is also maximum for tungsten complex.

4. Specific rotation of the complex when cerium nitrate was used was found to be higher than that when cerium chloride was used.

Our thanks are due to Mr. Jang Bahadur Jha for his kind help in the case of *e.m.f.* measurements.

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Catalytic Oxidation of Toluene in the Vapour Phase.

By J. K. Chowdhury and S. C. Choudhury.

Toluene may be oxidised in the vapour phase to benzaldehyde, benzoic acid or carbon dioxide and water according to conditions and nature of catalysts used. The reactions taking place may be represented by the following equations:

$$(1)\ C_6H_5{\cdot}CH_3 + O_2 = C_6H_5{\cdot}CHO + H_2O + 92800 \text{ cal.}$$
$$(2)\ C_6H_5{\cdot}CH_3 + 3O = C_6H_5{\cdot}COOH + H_2O + 162{,}500 \text{ cal.}$$
$$(3)\ C_6H_5{\cdot}CH_3 + 9O_2 = 7CO_2 + 4H_2O + 934{,}400 \text{ cal.}$$

Traces of anthraquinone may also be formed but the amount being very small, it is left out of consideration in this work. It is evident from the above equations that low temperature and excess of oxygen will favour the formation of carbonic acid, high temperature and less oxygen will favour aldehyde formation, while moderate temperature will be necessary for benzoic acid. It will be seen from the experimental data that this is actually the case, though very high temperature and prolonged contact with the catalyst favour complete combustion of toluene.

Different catalysts have been used by different investigators for the partial combustion of toluene and other aromatic hydrocarbons. Thus, metallic platinum was used by Coquilon (*Compt. rend.*, 1875 **80**, 1089), and by Wood and others (*ibid.*, 1907, **145**, 127). Oxides of nickel and cobalt were also found useful (F. P. 379725, 1907) while oxide of vanadium either alone or mixed with molybdenum trioxide and other oxides was found particularly suitable by Walter (*J. pr. Chem.*, 1892, **45**, 107) Gibbs (*Ind. Eng. Chem.*, 1919, **11**, 1031) and others, while Maxted (*J. Soc. Chem. Ind.*, 1928, **47**, 431 used tin vanadate as catalyst. Various catalysts have been used in these investigations and satisfactory results have been obtained with tin vanadate, specially when mixed with silica gel, alumina or active carbon.

In carrying out the oxidation, the following procedure was adopted. The reaction tube consisting of a glass combustion tubing ($2\frac{3}{8}' \times 1''$), packed in the middle with about 10 c.c. of the catalyst in the form of small porous granules, was heated in an electric furnace, the temperature of which was regulated by a rheostat and noted with a thermometer with a bulb placed in the catalyst bed. Air freed from carbon dioxide was passed with the help of a Cenco blower after dividing it into two sections, primary and secondary, each being measured separately with the flowmeter. The quantity of air was controlled by regulating the speed of the motor and by means of pinch-cocks placed on the passage. The flask containing a constant volume of toluene was heated in a thermostat, the primary air passed through the flask and laden with toluene vapour entered the reaction chamber. Just before entrance into the reaction tube, the toluene laden primary air was mixed with secondary air, heated in an oil-bath. The tube connecting the flask and the reaction tube was coiled with nicrom wire and heated electrically to prevent condensation of toluene vapour.

The products of oxidation were led through a test tube constricted at the centre and plugged with glass wool and perforated at the closed end. Benzoic acid collected in the constricted portion of the tube while benzaldehyde and carbonic acid passed through the perforations and were absorbed by standard baryta solution. Benzaldehyde was estimated in this solution by the addition of $KHSO_3$ (Sutton, "Volumetric Analysis", p. 311) while carbonic acid was estimated from the precipitate consisting of barium carbonate with the help of Schroedter apparatus. Benzoic acid deposited in the constricted tube was estimated by extraction with neutral rectified spirit aud titration with alkali. When the rate of flow of toluene vapour was rather fast, a small portion of benzoic acid passed out and dissolved in the baryta solution. This portion of benzoic acid was estimated by titrating the clear baryta solution with hydrochloric acid.

The quantity of toluene passing through the reaction tube was obtained from the difference in the weight of the flask containing toluene before and after each experiment.

The preparation of the catalysts and their incorporation with supports are dealt with later. Only pure Kahlbaum chemicals were used for the purpose.

Study of Nickel Catalysts.

Nickel oxide.—As very meagre practical details of the work of Wood, who obtained small quantities of benzaldehyde from toluene with nickel oxide as catalyst, are available we re-investigated the catalytic properties of nickel oxide.

A solution of pure nickel nitrate was precipitated with excess of pure caustic soda which was added very slowly with constant stirring. The precipitate was thoroughly washed with distilled water and dried at 110° and made into a large number of small pills in the moist state by application of minimum pressure between the fingers, so that the pills might retain a loose spongy structure. The pills were then packed between asbestos fibres and dried at 200°. It will be seen from the experimental data given in the following table that nickel oxide is not very active below 280°, the yield of benzaldehyde is fairly good but that of benzoic acid very poor. As is to be expected, the yield of benzaldehyde rises with temperature and liberal supply of air.

TABLE I *a*.

Catalyst—Nickel oxide. Volume of the catalyst space = 10·5 c.c. Temp. of thermostat = 45°. Temp. of the secondary air = 70°.

		Space Velocity.		Products on toluene used.		
Run No.	Temp.	Primary air.	Secondary air.	Benzoic acid.	Benzaldehyde.	CO_2
1	290°	300	800	2%	6·3%	...
2	320	400	1000	3·1	7·2	4·8%
3	320	500	1200	4·3	7·8	3·4
4	320	500	1500	6·9	7·6	2·9
5	320	800	1700	5·8	7·9	1·3

TABLE I *b*.

Values calculated from data of Table I*a*.

		Products on toluene attacked.			
Run No.	Toluene attacked.	Benzoic acid.	Benzaldehyde.	CO_2	Toluene destroyed.
2	10·03 %	31 %	72 %	48 %	14·4 %
3	11·03	39·1	70·9	30 9	9·2
4	12·66	54	59·8	22·8	6·84
5	11·6	50	68·1	11·2	3 36

Run number gives the number of successive runs with the same catalyst and indicates the efficiency of a catalyst on continued use.

Space velocity :—The velocity of all air currents is expressed as space velocity, namely, c.c. per hour per c.c. of the catalyst space.

(b) *Metallic nickel mounted on alumina.*—A mixed solution of pure nickel and aluminium nitrates was precipitated with excess of caustic soda, washed thoroughly and dried at 120°. 20 G. of these materials in the form of pills were packed between asbestos fibre and reduced in a current of hydrogen for about 24 hours.

It will be noted from Table II that yields of benzoic acid and benzaldehyde are not satisfactory when the rate of flow is increased. Toluene passes through the catalyst layer unoxidised, while too low a velocity causes complete combustion.

TABLE II.

Catalyst—Metallic nickel mounted on alumina. Volume of the catalyst space=10 c.c. Temp. of toluene bath=50°. Temp. of the secondary air=75°.

Temp.	Primary air.	Secondary air.	Benzoic acid on toluene used.
280°	500	1100	2·5 %
290	200	500	7·5
290	500	1100	8·5
300	200	500	9·1
330	200	500	8·9
330	200	500	8·9

(c) *Partly reduced nickel oxide.*—The oxide was prepared in the usual manner, dried at 110° and reduced in a current of hydrogen at 310°. It was found that little improvement was attained by reduction of the oxide for 15 hours but much better results were obtained by partial reduction of nickel oxide in a slow current of hydrogen for 3 to 4 hours only.

It appears that the presence of small amount of lower oxide of nickel is favourable for catalysis. It was apprehended that the lower oxide would be easily oxidised to the higher state in the presence of air and the activity of the catalyst would suffer but as the figures for repeated runs will show (Table III *a*), this apprehension has proved groundless. Once the reaction is started, the lower oxide is evidently reformed by the oxidation of toluene vapour.

TABLE III *a*.

Catalyst—Nickel oxide reduced in a slow current of hydrogen for 3 to 4 hours at 310°. Volume of the catalyst space=10 1 c.c. Temp. of the thermostat=45°. Temp. of the secondary air=70°.

Run No.	Temp.	Space velocity Prim. air.	Sec. air.	Products on toluene used. Benzoic acid.	Benzaldehyde.	CO_2.
1	290°	800	800	5·2%	11·7%	5·9%
2	290	800	1700	10·8	8·1	2·4
3	320	800	1700	11·3	8·9	9·1
4	„	1000	2500	16·8	10·2	0·05
5	340	„	„	20	13·1	0·12
6	„	1500	3500	18·9	12·1	...
7	420	1500	3500	10·1	16·1	8·6
8	450	1500	3500	9·6	18·1	14·9
9	450	„	„	8·2	17·6	14·1
10	„	1000	2500	5·7	15·9	17·4

TABLE III *b*.

Run No.	Toluene attacked.	Products on toluene attacked. Benzoic acid.	Benzaldehyde.	CO_2.	Toluene destroyed.
1	15·85 %	35·2 %	73·6 %	30·8 %	9·24 %
2	15·87	67·9	50·9	15	4·5
4	21·624	77·8	47·2	0·2	0·06
5	26·75	74·6	48·8	0·4	0·12
7	27·984	36	57·5	30·7	9·21
8	24·417	39·3	74·2	61	18·3
10	23·328	24·4	68·2	74·6	22·3

(*d*) *Partly reduced nickel oxide mounted on alumina.*—Still better results were obtained by incorporation of slightly reduced nickel oxide with small quantities of alumina. The activity of the nickel-alumina catalysts, however, varied according to the proportion of nickel and aluminium. From a solution of nitrates nickel and aluminium were precipitated with caustic soda, washed carefully and dried at 110°. It was then reduced in a current of hydrogen for $3\frac{1}{2}$ hours at 310° and cooled in a current of hydrogen. It was found that the presence of 10—20 % alumina in a mixed catalyst gave the most satisfactory results. By varying the temperature either the acid or the aldehyde could be obtained in good yields. The lower temperature (320—40°) is favourable for acid formation while higher temperature (420—50°) is suitable for the formation of aldehyde. The difference of 100° is great enough to allow regulation of temperature to obtain either the acid or the aldehyde as the main product. In the following Table IV *a* the data obtained with only one alumina-nickel catalyst are given though several such mixtures were tried as catalysts.

TABLE IV *a*.

Catalyst—20% alumina and 80% partly reduced nickel oxide. Volume of the catalyst space=10·2 c.c. Temp. of the thermostat=50°. Temp. of the secondary air=70°.

		Space velocity		Products on toluene used		
Run No.	Temp.	Prim. air.	Sec. air.	Benzoic acid.	Benzaldehyde.	CO_2.
1	295°	600	1500	14·2 %	...	...
2	295	500	1000	14·3	...	...
3	300	1200	2500	18·3	...	...
4	320	1500	3000	28·7	...	...
5	320	1200	2500	20·8	...	...
6	340	1500	3100	33·1	8·3 %	...
7	340	,,	,,	31·4	7·9	0·2 %
8	420	,,	,,	14·8	12·4	14·3
9	450	,,	,,	9·9	12·9	13·3

TABLE IV b.

Run No.	Toluene attacked.	Benzoic acid.	Benzal-dehyde.	CO_2.	Toluene destroyed.
	Products on toluene attacked				
6	82·046 %	103·4 %	26 %	...	...
7	30·483	102·9	25·9	0·6 %	0·18 %
8	26·178	56·4	47·3	54·5	16·35
9	24·138	41·2	58·7	76·2	22·8

Study of Vanadium Catalysts.

(a) *Aluminium vanadate.*—In view of the encouraging result obtained by mounting partly reduced nickel oxide on alumina, we applied this support to the well known catalyst vanadium pentoxide whose high activity has already been referred to.

To a solution of pure aluminium nitrate an excess of a solution of sodium vanadate was slowly added with constant stirring. The precipitate was washed, thoroughly dried at 110° and formed into porous globules. It will be observed that the yield of either the acid or the aldehyde is not up to expectation.

TABLE V a.

Catalyst—Aluminium vanadate. Volume of the catalyst space =11·6 c.c. Temp. of the thermostat=50°. Temp. of the secondary air=65°.

Temp.	Space velocity.		Yield of products on toluene used		
	Prim. air.	Sec. air.	Benzoic acid.	Benzaldehyde.	CO_2.
280°	200	500	26·02 %	4·8 %	1·1 %
,,	,,	,,	18·3	4·1	1·8
320	,,	,,	20·4	8·3	4·1
,,	,,	,,	19·2	8·6	3·9
330	200	500	23·8	10·3	4·3
350	300	700	24·8	4·2	1·3
360	400	900	24·4	10·8	2·1
450	,,	,,	8·5	11·2	3·7
,,	1000	2500	8·9	11·8	0·56

TABLE V *b*.

Toluene used.	Products on toluene attacked			Toluene destroyed.
	Benzoic acid.	Benzaldehyde.	CO_2.	
19·5%	102·6%	24·6%	5·1%	1·51%
23·7	86	35·4	17·3	5·19
23·05	83·4	37·8	16·96	5·088
28·1	85	36·9	15·8	4·59
17·23	48·4	65·2	21·7	6·51
22·64	109·7	18·5	5·7	1·67

(*b*) *Vanadium pentoxide incorporated with silica gel.*—Hydrochloric acid (*d* 1·05) was added drop by drop to a concentrated solution of sodium silicate with mechanical stirring. After washing, the precipitate was incorporated with a solution of ammonium vanadate and rubbed well in a mortar. It was dried first on water-bath and finally at 110° and was used in the form of small porous balls. It will be observed from Table VI *a* that the results are more promising than any obtained previously. A maximum of 41·2% benzoic acid is obtained at 290°, the rate of flow of primary air being 200 and secondary air 500. On raising the temperature and the rate of flow of primary and secondary air, benzaldehyde is obtained in large amounts. Reduction of the rate of flow favours complete combustion.

TABLE VI *a*.

Catalyst—Silica gel and vanadium oxide. Volume of the catalyst space=10·6 c.c. Temp.=50°. Temp. of the secondary air=75°.

Run No.	Temp.	Space velocity.		Yield of products on toluene used		
		Prim. air.	Sec. air.	Benzoic acid.	Benzaldehyde.	CO_2.
1	280°	200	500	38 %	2·8%	8·8%
2	290°	200	500	41·2	3	8·9
3	290°	500	1500	26	7·9	3·1
4	290°	200	500	40·1	3·2	9·0
1	320°	200	500	37·9	3·1	10·9
2	320°	600	1200	32·8	6·4	5·2
3	430°	600	1200	10·3	11·2	27·2
4	,,	1200	2500	8·7	15·9	10·1
5	,,	1200	2400	8·3	15·1	8·9
6	,,	1200	2400	8·9	14·6	9·1
7	,,	200	500	1·2	3·8	50·6

TABLE VI *b*.

Run No.	Toluene attacked.	Products on toluene attacked Benzoic acid.	Benzaldehyde.	CO_2.	Toluene destroyed.
2	36·17%	118·8%	8·2%	24·5%	7·35%
3	35·55	112·6	8·9	25·2	7·54
1	34·38	110·1	9·0	31·7	6·51
2	31·728	108·4	20·18	16·4	4·92
3	25·62	40·2	48·7	106·2	31·26
4	19·386	6·2	19·5	260·8	78·0

(c) *Tin vanadate as catalyst.*—To a solution of tin chloride a solution of sodium vanadate was added slowly till precipitation was complete. The product was thoroughly washed, dried at 110° and was used in the form of porous pills. The results prove the high activity of tin vanadate, a maximum of about 45% benzoic acid having been obtained.

The yield of aldehyde was 14·1% at 450°. The difference of temperature is, therefore, sufficiently great to regulate the yield of either benzoic acid or benzaldehyde. If the rate of flow is moderate, complete combustion to carbon dioxide takes place at this high temperature.

TABLE VII *a*.

Catalyst—Tin vanadate. Volume of the catalyst space = 10·6 c.c. Temp. of the thermostat = 45°. Temp. of the secondary air = 75°.

Run No.	Temp.	Space velocity Prim air.	Sec. air.	Yield of benzoic acid on toluene used.
1	270°	200	500	25%
2	,,	300	800	17
3	,,	200	500	23
4	280	200	500	40·4
5	290	200	500	45
6	290	500	1100	36
7	,,	200	500	44·2
8	,,	200	500	45·1

TABLE VII *b*.

Run No.	Temp.	Space velocity Prim. air.	Sec. air.	Yield of products on toluene used Benzoic acid.	Benzaldehyde.	CO_2.
6	320°	200	400	20·2%	4·2%	28·3%
7	,,	900	2000	18·3	6·84	12·6
8	380°	,,	,,	9·7	9·3	25·8
9	420°	,,	,,	8·4	11·6	30·5
10	450°	,,	,,	1·6	12·3	36·5
11	,,	1200	1500	1·95	18·8	20·01
12	,,	1500	3500	2·2	14·1	9·2
13	,,	200	500	nil	6·3	48·3

TABLE VII *c*.

Run No.	Toluene attacked.	Products on toluene attacked Benzoic acid.	Benzaldehyde.	CO_2.	Toluene destroyed.
6	27·29%	73·99%	15·5%	103·6%	31·08%
7	23·45	77·8	29·1	54·7	16·41
8	23·106	42·1	40·4	112·1	33 63
9	25·542	32·9	41·5	119·6	35·58
10	22·85	6·9	53·7	159·4	47·8
12	16·67	13·1	84·4	55	16·5
13	19·97	...	31·5	241·5	72·45

Tin vanadate mounted on silica gel.—The activity of tin vanadate could be further increased by mounting it on silica gel. To a concentrated solution of sodium silicate, hydrochloric acid (*d* 1·05) was added drop by drop with constant stirring. The silica gel obtained was carefully washed and suspended in a solution of tin chloride and a solution of sodium vanadate was added until tin vanadate was completely precipitated and incorporated with silica gel. The mixed pricipitate was used in the form of porous ball as usual.

TABLE VIII *a*.

Catalyst—20% silica gel and 80% tin vanadate. Volume of the catalyst space=10·7 c.c. Temp. of the thermostat=45°. Temp. of the secondary air=70°. Temp. of the reaction=295°.

Run No.	Space velocity Prim. air.	Sec. air.	Yield of benzoic acid on toluene used.
1	200	500	50·9%
2	,,	,,	56·1
3	,,	,,	57·8
4	,,	,,	55·9
5	,,	800	40·1
6	,,	1200	34·8

TABLE VIII *b*.

Catalyst—10% silica gel and 90% tin vanadate. Volume of the catalyst space=10·6 c.c. Temp. of the thermostat=45°. Temp. of the reaction=295°.

Run No.	Space velocity Prim. air.	Sec. air.	Yield of benzoic acid on toluene used.
1	200	500	52%
2	200	500	56
3	200	500	55·1
4	300	2000	32·3

TABLE VIII *c*.

Catalyst—50% tin vanadate and 50% silica gel. Volume of the catalyst space=10·8 c.c. Temp. of the thermostat=45°. Temp. of the reaction=295°.

Run No.	Space velocity Prim air.	Sec. air.	Yield of benzoic acid on toluene used.
1	200	500	14%
2	200	500	16
3	200	500	18·1
4	200	500	15·8
5	300	1000	10·6

TABLE VIII *d*.

Catalyst—30% tin vanadate and 70% silica gel. Volume of the catalyst space = 10·3 c.c. Temp. of the thermostat = 45°. Temp. of the reaction = 295°.

Run No.	Space velocity Prim air.	Sec. air.	Yield of benzoic acid on toluene used.
1	200	500	6·1%
2	200	500	5
3	200	500	7
4	200	500	5·8

From the above experimental data, it will be clear that highly porous alumina and silica serve more as promoters than as mere supports for nickel and vanadium catalysts. The activities are higher than those calculated from the composition of the constituents on the supposition that the activity of one is independent of the other. The efficiency of vanadium oxide and tin vanadate can be increased by addition of a small amount of silica gel, while the activity of partly reduced nickel oxide can similarly be increased by the addition of small amounts of alumina. This is particularly significant as nickel catalyst is comparatively cheap and the activity of mixed nickel alumina catalyst is considerable though not equal to that of vanadium catalyst.

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Chemical Investigation of the High Boiling Bases from Anthracene Oil.

By S. K. Ganguli and P. C. Guha.

No systematic investigation regarding the isolation and identification of the high boiling bases occurring in anthracene oil appears to have been made so far, though 3:5- and 2:4-dimethylpyridines, 1-amino-2:4-dimethylpyridine, 2:3:6 trimethylpyridine, 2-methyl-4-ethylpyridine (Eckert and Loria, *Monatsh.*, 1917, **38**, 225), 2:3:4:5-tetramethylpyridine, 2:5-dimethylpyridine (Ahrens, *Ber.*, 1904, **37**, 2062), 2:6-dimethylpyridine (Heap Jones and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936), quinoline (Runge, *Pogg. Ann.*, **31**, 68), *iso*quinoline (Hoogewerff and van Drorp, *Rec. trav. chim.*, 1885, **4**, 125; 1886, **5**, 305), quinaldine (Jacobsen and Reimer, *Ber.*, 1883, **16**, 1082), lepidine (Williams, *J. Chem. Soc.*, 1863, **16**, 431), acridine (Grabe and Caro, *Annalen*, 1871, **158**, 265) and hydroacridine (Decker and Dunant, *Ber.*, 1909, **42**, 1178) have been isolated.

Considering the manifold importance of pyridine and quinoline derivatives such as their application as starting materials for the synthesis of alkaloids and their derivatives, use of quinoline derivatives like thaline (6-methoxytetrahydroquinoline), kairoline (*N*-ethyltetrahydroquinoline), kairdine (1-oxy-*N*-methyltetrahydroquinoline), plasmoquin, analgen (*N*-acetyl-3-methoxyquinoline) in chemotherapy, their use as intermediates in the photosensitising dyes of cyanine class and so on, and also considering the possibility of yet undiscovered bases occurring in anthracene oil exhaustive investigation of the bases from anthracene oil was taken in hand.

The bases from anthracene oil (b.p. 270—350°) were extracted with moderately dilute hydrochloric acid, the acid extract freed from admixed neutral substances by steam distillation and finally the bases liberated with sodium hydroxide. The bases consist of a mixture of extraordinary complexity, the separation of the individuals by fractional distillation under atmospheric pressure was not possible as they show signs of decomposition. Their isolation by fractional distillation under highly reduced pressure was not success-

ful, as is indicated by the fact that fractions collected even within one degree's range did not yield crystalline salts with acids or double salts with $ZnCl_2$, $HgCl_2$, etc.

The above methods having failed, the possibility of conversion of these bases by oxidising the alkyl groups into carboxyl groups and then to isolate the individual carboxylic acids by fractional crystallisation was considered. The fraction 180—200°/30 mm., on oxidation with chromic acid mixture according to the method of Weidel (*Ber.*, 1879, 12, 1992) gave a water-soluble resinous mass from which no individual acid could be isolated. Phenyl phenacyl esters of these acids (*cf.* Drake and Bronitsky, *J. Amer. Chem. Soc.*, 1930, 52, 3718) have, however, yielded three nitrogen containing compounds I, II, and III melting respectively at 208°, 201° and 101°.

$$R{\cdot}CH_3 \longrightarrow R{\cdot}CO_2H \longrightarrow R{\cdot}CO_2Na + BrCH_2{\cdot}CO{\cdot}C_6H_4{\cdot}C_6H_5 \longrightarrow$$

$$RCO{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}C_6H_5 + NaBr \text{ (R=the basic radicle)}$$

The quantity of these esters was not sufficient to allow their conversion into the respective acids; their identification (*cf.* Drake and Bornitsky, *loc. cit.*) was not possible due to the non-existence of similar phenylphenacyl esters of pyridine, quincline and *iso*quinoline carboxylic acids. From the analytical value (N, 2·16) compound I appears to be phenylphenacyl ester of quinoline dicarboxylic acid.

Subsequently the bases were distilled under highly reduced pressure with fractionating column (rod and disc type) and 21 different fractions, each coming within a range of 5° were separately collected. The low boiling bases consisting of quinoline and homologues of pyridine were fractionated between 75—100°/5 mm. and the higher fractions between 80—160°/2 mm. Detailed investigation of the bases distilling above 100°/2 mm. was taken up, their boiling point under ordinary pressure being higher (above 250°) than those of the pyridine and quinoline bases already isolated from this source. Isolation of the individuals (*a*) from sulphuric acid solution by fractional precipitation with ammonia, (*b*) as their double salts with $ZnCl_2$, $HgCl_2$, copper acetate, etc., and (*c*) as hydrochloride, sulphate, chromate, acetate, oxalate, tartrate, salicylate was not successful. Their isolation by fractional crystallisation of the amorphous salts formed with methylene disalicylic acid according to the methed described in Indian Patent No. 14616 (July, 1928) for the separation of alkaloids, was tried with no better result.

The picrates of the bases contained in the fracions b.p.80·5—110°/2mm. separated as a yellow crystalline mass whereas those of the fractions 110—5—160°/2 mm. were tarry semi-solid products. Isolation of the individual picrates from fractions 100—05°/2mm. and 105—10°/2mm. was not possibly even after repeated fractional crystallisation. This difficulty was, however, overcome taking recourse to a process of regulated cooling within a range of 10° in a thermostat. Following this process of fractional crystallisation for more than 100 times, it has been possible to isolate three individual picrates (IV, V, VI) from the fraction 100—05°/2 mm. and four picrates (VII, VIII, IX, X) from the fraction 105—10°/2 mm. of which X is identical with VI.

	Colour and crystalline nature.	M.p.	Composition of	
			Picrates.	Bases.
IV	Greenish yellow shining rectangular plates	230°	$C_{17}H_{14}O_7N_4$	$C_{11}H_{11}N$*
V	Yellow microcrystalline plates	181°	$C_{16}H_{12}O_7N_4$	$C_{10}H_9N$*
VI	Dirty green needles	212°	$C_{17}H_{14}O_7N_4$	$C_{11}H_{11}N$
VII	Greenish yellow thick needles	201°	$C_{16}H_{12}O_7N_4$	$C_{10}H_9N$
VIII	Dull yellow needles	203°	$C_{17}H_{14}O_7N_4$	$C_{11}H_{11}N$*
IX	Yellow shining plates	198°	$C_{17}H_{14}O_7N_4$	$C_{11}H_{11}N$

The melting point of the picrates (IV) and (VII) suggested their identity with those of 4:6-dimethylquinoline (m.p. 230°) and 8-methylquinoline (m.p. 200°). But the depression in their mixed melting points with the picrates of the synthetic 4:6-dimethyl- and 8-methylquinolines indicated their difference. Picrate (IX) was, however, proved to be identical with that of synthetic 5:8-dimethylquinoline (m.p. 198°).

The fee bases have been liberated from the individual picrates by the action of alkali, the yield in no case was sufficient for determination of their boiling points. The bases liberated only from three of these picrates (VI, VII, IX) could, however, be analysed but the bases from all of the picrates have been converted into crystalline platinic chloride double salts *via* hydrochlorides. The ease with

* These values are calculated from the nitrogen content of the picrates and platinum content of the platinic chloride double salts.

which these are formed and their sharp melting points only indicate the purity and individuality of the free bases.

Of the fourteen possible monomethylquinolines (7) and *iso*quinolines (7) only 5- and 7-methyl*iso*quinolines are not known. It appears likely that the two bases corresponding to (V) and (VII) represent the two missing monomethyl*iso*quinolines.

As out of the 42 possible dimethyl derivatives of quinoline (21) and *iso*quinoline (21) only about 13 are known, it is not easy to identify the three new dimethyl bases corresponding to the picrates (IV, VI, VIII).

As there is no alkyl quinoline or *iso*quinoline base known the melting point of whose picrate approaches near that of (IV), (VI), and (VIII) and and as the composition of the bases agrees with those of monomethyl- or dimethylquinolines or *iso*quinolines, it is claimed that five new bases have been isolated from anthracene oil, the presence of 5:8-dimethylquinoline in anthracene oil is also established.

Experimental.

Extraction of the bases.—Anthracene oil (20 gals.) was extracted by shaking each time 2 litres of the oil with hydrochloric acid (1 litre, 12%) in a shaking machine for 3 hours. The acid extracts were subjected to steam distillation to eliminate the neutral and phenolic bodies mechanically carried over during extractions. The bases were precipitated with caustic soda, washed with water and dried, yield 1784 g.

Oxidation of the bases to their carboxylic acids.—The bases (56 g.) boiling at 180—200°/30 mm. were dissolved in sulphuric acid (25%, 135 c.c.) to which an additional quantity of sulphuric acid (448 c.c.) diluted with water (840 c.c.) was added. Chromic acid (280 g.) dissolved in water (280 c.c.) was gradually added to the acid solution of the bases cooled in ice with stirring. The reaction mixture was allowed to attain the laboratory temperature during 12 hours, and then kept in a thermostat at 70° for 4 days, till the solution became green. Chromium was freed as hydroxide by ammonia, sulphuric acid in the filtrate was removed by baryta and then the excess of baryta by carbon dioxide. Dilute sulphuric acid was carefully added to the solution of the barium salts and the precipitated barium sulphate removed. The free carboxylic acids obtained from above on concentration were obtained only as

a resinous semi-solid mass. The yield of the mixed acids was 12·56 g.

p-*Phenylphenacyl esters of the acids.*—The mixed acids were dissolved in alcohol and the volume made up to 250 c.c. with water; 142 c.c. of this acid solution required for neutralisation 180 c.c. of sodium hydroxide solution (0·1653 *N*). *p*-Phenylphenacyl bromide (8·2 g.) dissolved in alcohol (50 c.c.) was added to a concentrated solution of the above sodium salt and the mixture heated under reflux for 2 hours. The contents of the flask were then cooled, filtered and the residue freed from sodium bromide. The white solid, so obtained, however, did not melt sharply and yielded on repeated fractional crystallisation from a mixture of chloroform and alcohol, three distinct compounds melting respectively at 208°, 201° and 101°; the first contains N, 2·16, $C_{39}H_{27}O_6N$ requires N, 2·31 per cent.; the quantity of the second and the third were not sufficient for analysis.

Fractional distillation under reduced pressure.—The bases (1620 g.) were fractionated into two portions (A) up to 150°/10 mm. (764 g.) and (B) above 150°/10 mm. (850 g.). The fraction (A) was fractionally distilled at 10 mm and distillate collected separately within a range of 10°. Each of these fractions was refractionated at 5 mm. and the distillates coming within the range of 5° separately collected, the residue from preceding fractions being mixed with the fraction to be distilled next. (B) was similarly fractionated at 2 mm. and the distillate collected within a range of 10° first and then again within 5° as in the case of (A). In the following table are shown the different fractions collected from (A) as obtained in the second series of distillations at 5 mm. with their refractive indices, densities and yields.

TABLE I.

Fraction.	Temp.	n_D^{40}	D_{40}^{40}.	Distillate.
	Bases boiling below 75°			6·15%.
1	75-80°	1·5720	1·0294	4·84
2	80-85	1·5948	1·0585	7·81
3	85-90	1·6019	1·0661	15·00
4	90-95	1·6061	1·0706.	8·36
5	95-100	1·6039	1·0780	8·04

Table II indicates the different fractions obtained from residues of (A) and the high boiling bases of (B) collected at 2 mm pressure together with their refractive indices, densities and yields.

TABLE II.

Fraction.	Temp.	n_D^{40}	D_{40}^{40}	Distillate.
1	80-85°	1·6051	1·0753	2·23%
2	85-90	1·6076	1·0753	2·86
3	90-95	1·6058	1·0778	4·28
4	95-100	1·6055	1·0783	5·65
5	100-05	1·6072	1·0794	4·64
6	105-10	1·6071	1·0802	2·55
7	110-15	1·6019	1·0812	0·74
8	115-20	1·6051	1·0819	0·47
9	120-25	1·6105	1·0919	0·68
10	125-30	1·6289	1·1074	2·01
11	130-35	1·6448	1·1085	2·15
12	135-40	1·6445	1·1125	0·68
13	140-45	1·6448	1·1358	0·89
14	145-50	1·6588	1·1415	0·45
	150-55	1·6550	1·1424	0·80
16	155-60	1·6511	1·1450	0·28
	Residue			18·35

Separation of the bases as their picrates.—All the 21 fractions (Table I and II) gave picrates, those obtained from the fractions 1 to 5 (Table I) as also from 1 to 6 (Table II) were yellow crystalline solids and melt within a wide range of temperature. Picrates from fractions 7—16 (Table II) came as brownish-black tarry products. The individual picrates were isolated from fractions 100—105°/2 mm. and 105—110°/2 mm. by repeated fractional crystallisation from alcohol by regulated cooling within a range of 10° in a thermostat and the melting points of all the fractions carefully recorded, till the m.p. of any particular fraction was within a range of 1° and remained unaltered on further crystallisation.

Picrates from fraction b.p. 100-105°/ 2 mm. (5, Table II).—To the bases (40 g.) dissolved in glacial acetic acid (850 c.c.) was added picric acid (50 g.) dissolved in glacial acetic acid (850 c.c.). The mixture was warmed on a water-bath and then allowed to cool when the picrates separated as a yellow crystalline mass, m.p. 170—85°.

- R
  - R_1
    - R_2
      - R_3
        - R_4
          - R_5
            - R_6
            - SR_5
          - . . .
          - SR_4
            - $R(SR_4)$
            - $S(SR_4)$
        - SR_3
          - $R(SR_3)$
            - $R(RSR_3)$
            - $S(RSR_3)$
          - $S(SR_3)$
            - $R(SSR_3)$
            - $S(SSR_3)$
      - SR_2
        - $R(SR_2)$
          - $R(RSR_2)$
            - $R(RRSR_2)$
            - $S(RRSR_2)$
          - $S(RSR_2)$
            - $R(SRSR_2)$
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            - $S(RSSR_2)$
          - $S(SSR_2)$
            - $R(SSSR_2)$
            - $S(SSSR_2)$
    - SR_1
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Explanation of the chart.—R indicates residue, S indicates solution; R_1 and S_1 mean respectively residue and solution from R on crystallisation. R_2 and SR_1 mean respectively residue and solution from R_1. Similarly RS_1 and SS_1 mean respectively residue and solution from S_1; $R(RS_1)$ and $S(RS_1)$ mean respectively the residue and solution from RS_1 crystallised and so on.

The *picrate* (IV) was isolated from the residue R_5 as greenish-yellow rectangular plates, m.p. 230°, yield 0·52 g. (Found: N, 14·52. $C_{17}H_{14}O_7N_4$ requires N, 14·76 per cent). The mixed melting point with the picrate (m.p. 230°) of 4:6-dimethylquinoline, prepared from *p*-toluidine and methylene acetone (*Annalen*, 1890, **245**, 360), was below 200°. The platinic chloride double salt made from the hydrochloride of the free base (oil), obtained from the picrate by the action of potassium hydroxide and extraction with ether, crystallised from water as dull yellow needles, m.p. 220°. (Found: Pt, 26·95. $[C_{11}H_{11}N, HCl]_2 PtCl_4$ requires Pt, 26·95 per cent).

The *picrate* (V) isolated from the residue indicated as $R(SR_2)$ and also from $R(RRRSR_1)$ separated as yellow microcrystalline plates, m.p. 181°, yield 1·56 g. (Found: N 15·81. $C_{16}H_{12}O_7N_4$ requires N, 15·05 per cent). The *free base*, liberated from the picrate, was a thick colourless oil and became coloured in contact with air. The *platinic chloride double salt*, obtained from the hydrochloride, crystallised from water as yellow microneedles, m. p. 202-3°. (Found: Pt, 28·35. $[C_{10}H_9N,HCl]_2$ Pt Cl_4 requires Pt, 28·02 per cent).

The *picrate* (VI) was isolated from $R(RRRRS_1)$ and $R(RSRRS_1)$ as dirty green needles, m.p. 212°, yield 2·35 g. (Found: N, 14·42. $C_{17}H_{14}O_7N_4$ requires N, 14·76 per cent). The *free base* contained N, 9·02. $C_{11}H_{11}N$ requires N, 8·91 per cent. The *platinic chloride double salt* crystallised from water in orange-yellow needles, m.p. 256-57° (decomp.). (Found: Pt, 27·01. $[C_{11}H_{11}N, HCl]_2 PtCl_4$ requires Pt, 26·95 per cent).

Isolation of the individual picrates from fraction b.p. 105—110°/2 mm. (6, Table II) was effected similarly as from fraction 100—5°/2 mm.

The *picrate* (VII) was isolated from the residue R_4 as greenish-yellow thick needles, m.p. 201°; yield 2·54 g. (Found; N, 14·82. $C_{16}H_{12}O_7N_4$ requires N, 15·05 per cent). The mixed melting point with the picrate (m.p. 200°) of 8-methylquinoline, prepared from *o*-toluidine (Skraup, *Monatsh*, 1881, **2**, 153) was below 175°.

The *free base* separated as a thick colourless oil and emitted pungent smell at 100°. (Found: N, 10·10. $C_{10}H_9N$ requires N, 9·79 per cent). The *platinic chloride double salt* crystallised from water in orange-yellow needles, m.p. 207°. (Found: Pt, 27·98. $[C_{10}H_9N, HCl]_2 PtCl_4$ requires Pt, 28·04 per cent).

The *picrate* (VIII) was obtained from $R(RSRSR_1)$ by one more crystallisation as needles, m.p. 203°; yield, 0·53 g. (Found: N, 14·58.

$C_{17}H_{14}O_7N_4$ requires N, 14·76 per cent). The *platinic chloride double salt* crystallised from water as yellow needles, m.p. 218° (decomp.). (Found: Pt, 26·98. $[C_{11}H_{11}N, HCl]_2PtCl_4$ requires Pt, 26·95 per cent).

The *picrate* (IX) was obtained from $R(RRSR_1)$ as yellow shining plates, m.p. 198°, yield 2·84 g. (Found: N, 14·59. $C_{17}H_{14}O_7N_4$ requires N, 14·76 per cent). The mixed melting point with the picrate (m.p. 198°) of 5:8-dimethylquinoline prepared from 1:4:2-xylidine (Berend, *Ber.*, 1885, **18**, 3165) was undepressed proving their identity. The *free base* is a colourless oil. (Found: N, 8·68. $C_{11}H_{11}N$ requires N, 8·91 per cent). The *platinic chloride double salt* crystallised from water in yellow needles, m.p. 234° (decomp.). (Found: Pt, 26·81. $[C_{11}H_{11}N, HCl]_2PtCl_4$ requires Pt, 26·95 per cent). The *chromate* crystallised from water in orange-yellow needles, m.p. 149°. The mixed melting points of the platinic chloride double salt and the chromate with those of the synthetic base remained undepressed.

The *picrate* (VI) was also obtained from $R(RRRS_1)$ and was proved identical with the compound obtained from fraction b.p. (105°/2 mm.).

Summary.

1. The mixture of the sodium salts of the carboxylic acids obtained from the fraction b.p. 180—200°/30 mm. by oxidation, has yielded with phenylphenacyl bromide three distinct esters, m.p. 208°, 201° and 101°. The first one appears from its composition to be derived from quinoline or *iso*quinoline dicarboxylic acid.

2. The fractions b.p. 100—105°/2 mm. and 105—110°/2 mm. give a mixture of yellow crystalline picrates from which after repeated fractional crystallisations under regulated cooling within a range of 10°, it has been possible to isolate six distinct and individual picrates (IV—IX). All of these picrates have been converted into the platinic chloride double salts possessing sharp m.p. *via* the free base and the hydrochloride. From the analytical values of the free bases obtained from VI, VII and IX and the composition of the picrates and the platinic chloride double salts it is claimed that five new bases have been isolated from anthracene oil, the presence of 5:8-dimethylquinoline in it is also established.

Studies on the Decomposition and Reactions of Urea. Part IV. On the Mechanism of the Formation of Ammelide, etc.

By (Late) Jnanendra Mohon Das-Gupta.

Investigations on the mechanism of the formation of ammelide by the decomposition of urea by heat, have been found of interest from several points of view. Apart from the complex nature of this mechanism, which is by no means clear, closely related to this problem are probably (*i*) the origin of cyanuric acid from the decomposition of urea by heat, (*ii*) the mechanism of the reaction of biuret. Solution of the first problem might, therefore, throw light on the others and *vice versa*. The possibility of cyanuric acid being the precursor of ammelide which would be formed by the direct interaction of the former with ammonia is disposed of by the observation that ammelide is not obtained by heating cyanuric acid with urea below 180°, though under such condition urea is an excellent source of ammonia (Das-Gupta, *J. Indian Chem. Soc.*, 1933, **10**, 111, 117). The alternative explanatian due to Werner (*J. Chem. Soc.*, 1913, **103**, 2275), appears defective when certain facts are taken into consideration. His results would show that ammelide is formed below 180°. But with a more careful regulation of the temperature it is found that ammelide is not formed appreciably below 190°, under various conditions; while it is produced to an appreciable extent only at about 195°, which is the decomposition point of biuret. This would suggest that the formation of ammelide is probably preceded by the decomposition of biuret, its formation being then directly connected with the latter but not in the way shown by Werner.

The experiments described clearly establish the following facts:

(*i*) Though biuret is considerably formed between 150–180°, yet no ammelide is produced, although urea under such condition is an excellent source of cyanic acid (*loc. cit.*).

(*ii*) Taking into consideration that the ammonia evolved may interfere with the action of cyanic acid on biuret, the decompositions have been studied in an atmosphere of hydrochloric acid gas. Even under such condition no ammelide is formed below 185°.

(*iii*) Yield of cyanuric is very small below 190°, whereas at or above 195°, it is very considerable. Though a rise of 5° temperature should affect the polymerisation of cyanic acid to some extent, this alone cannot be regarded as sufficient to explain the considerable increase in the output of cyanuric acid, which therefore must be connected, to a great extent, with the decomposition of biuret.

(*iv*) Formation of ammelide is always accompanied by that of cyanuric acid but the reverse is not always true.

(*v*) Ammelide could not be obtained by passing cyanic acid gas (produced by the depolymerisation of cyanuric acid) over anhydrous biuret suspended in a finely divided state in dry benzene at 50-70° for half an hour.

The following scheme, it is hoped, would explain all these facts in a satisfactory way:

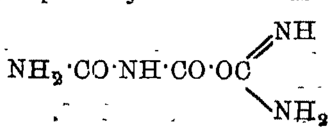
I. $NH_3 + \underset{\text{Dicyanic acid.}}{NH_2{\cdot}CO{\cdot}NCO} \leftarrow \underset{\text{Biuret.}}{NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2} \rightarrow NH_2{\cdot}CO{\cdot}NH_2 +$ NHCO

II. $\underset{\text{Dicyanic acid.}}{NH_2{\cdot}CO{\cdot}NCO} \xrightarrow{NH_2{\cdot}CO{\cdot}NH_2} \underset{\text{Hypothetical triuret.}}{NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$

Dicyanic acid $\downarrow$ NHCO

Hypothetical triuret $\downarrow$ Ammelide $+ H_2O$ $\quad\downarrow$ Cyanuric acid $+ NH_3$

The reactions I and II are typical of the substituted ureas (*cf.* Davis and Underwood, *J. Amer. Chem. Soc.*, 1922, **44**, 2595). The above mechanism would show that the yield of ammelide can not be large, at least not so much as that of cyanuric acid. This is actually the case. It also shows that the origin of cyanuric acid is not only due to the polymerisation of cyanic acid formed by the decomposition of urea but also possibly to three other sources namely, (*i*) decomposition of biuret into urea and cyanic acid, which latter then polymerises, (*ii*) dicyanic acid, (*iii*) hypothetical triuret (Behal, *Bull. Soc. chim.*, 1914, *iv*, **15**, 149). It may be noted here in this connection that carbonyl dicarbamide of Schiff (*Annalen*, 1896, **291**, 374), as it appears from its properties and mode of preparation, is probably constituted as follows:



It is quite natural to expect the formation of dicyanic acid as a result of the decomposition of biuret when it is remembered that most substituted ureas decompose in the two directions shown above. It has been found that dicyanic acid is formed from the decomposition of nitrobiuret (Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1801). A further evidence of such decomposition is afforded by the formation of phenylbiuret from the action of biuret on aniline. The latter reaction would appear to take place thus:

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + PhNH_2 \longrightarrow PhNH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_3$$

Sance, however, its formation is always accompanied by the simultanieous production of diphenylurea, the above simple mechanism is not sufficient. Evidently in the above reaction biuret undergoes decomposition first as in (I) and then reacts thus:

$$NH_2{\cdot}CO{\cdot}NCO + PhNH_2 \longrightarrow PhNH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$$

Dicyanic acid.

$$PhNH_2 + NHCO \longrightarrow PhNH{\cdot}CO{\cdot}NH_2 \longrightarrow PhNH{\cdot}CO{\cdot}NH{\cdot}Ph$$

It may be observed from the experiments described below, that though biuret decomposes at about 195° in the solid state, the decomposition point is much lowered in presence of aniline (150-80°). (*cf.* decomposition of urea in various solvents).

The formation of ammelide in the reaction of phosgne with ammonia (Hantzsch and Stuer, *Ber*, 1905, **38**, 1022; Werner, *J. Chem. Soc.*, 1918, **113**, 694) is not different to account for according to this view:

$$NH_2{\cdot}COCl + NHCO \longrightarrow NH_2{\cdot}CO{\cdot}NCO + HCl$$

Dicyanic acid.

$\downarrow$ Urea $\quad\downarrow$ NH_3

Triuret Biuret

$\downarrow$

Ammelide and cyanuric acid.

EXPERIMENTAL.

Decomposition of urea by heat.—Urea (5 g.) was heated in a weighed hard glass test tube (12 × 2 cm.) in an oil-bath to the desired temperature. It was then maintained at the temperature for 15 minutes

or more, as required, then cooled, weighed and from the difference the loss due to the escape of gases found out. The residue was dissolved in water (40-50 c.c.). Biuret was estimated colorimetrically by comparing with a standard solution (0·1%) and cyanuric acid by titration with $N/10$-alkali (phenolphthalein as indicator), after removing any ammonia present in the solution by blowing air through it (15 to 20 min.). In case there is a mixture of ammelide and cyanuric acid, these can be satisfactorily estimated by the following modification. An excess of measured volume of N-alkali was added to the mixture (obtained by adding 50 c.c. of water to the fused mass), so that a clear solution was obtained. An equal volume of a N-acid was then added, which threw down the ammelide, while the cyanuric acid remained completely dissolved. The precipitate is washed several times with cold water and the washings added to the filtrate. It is next dried and weighed. Cyanuric acid is estimated by titrating the filtrate with $N/10$- alkali and urea by adding nitric acid to a concentrated fraction of the same or from difference. In the experiments noted in Table III, urea (15 g.) was melted in a 100 c.c. conical flask and a slow current of dry HCl gas was directed on to the surface of the liquid (3-4 bubbles per minute).

TABLE I.

Action of heat on urea at different temperatures.

	170° for 15 mins.	180° for 15 mins.	180-85° for 15 mins.	190-95° for 15 mins.	150-160° for ½hr. and then at 200-10° for ½hr
Biuret	24·2%	28·3%	30·4%	23·3%	4·5%
Cyanuric	Trace	0·4	0·3	5·4	26·3
Ammelide	Nil	Nil	Nil	2·5	10·8
Urea	71·2	64·3	61·0	52·4	33·7
Loss (NH_3 + NHCO)	4·2	7·1	8·3	16·4	24·7

TABLE II.

Action of heat on urea for different periods.

Temperature = 170°.

	30 min.	45 min.	60 min.	75 min.	90 min.
Loss (NH_3 + NHCO)	2·1%	2·5%	3·4%	3·8%	5·2%
Sublimate (NH_4OCN)	2·3	4·2	5·0	6·1	7·3
Biuret	30·5	28·2	25·0	22·5	20·5
Cyanuric acid	0·1	0·12	0·14	0·18	0·2
Ammelide	Nil	Nil	Nil	Nil	Nil

TABLE III.

Action of heat on urea in an atmosphere of HCl.

	175° for 15 mins.	180° for 15 mins.	180-85° for 45 min.
Biuret	22·5%	21·9%	18·5%
Ammelide	Nil	Nil	Trace
Urea	63·0	60·1	55·2

Action of biuret on aniline.—Anhydrous biuret (3·4 g.) and aniline (3·1 g.) were heated together in an oil-bath to the desired temperature. The melt was extracted with warm water (30-40 c.c.) and filtered hot. The precipitate on crystallisation from alcohol yields diphenylurea, m.p. and mixed m.p. 235°. The filtrate, freed from aniline, was charcoaled, concentrated, cooled and treated with ether. From the ethereal solution, phenylbiuret crystallised out and was recrystallised from hot water, m. p. and mixed m.p. 165°. The aqueous solution on concentration to a small volume yields a small quantity of phenylurea, m.p. 145°.

	160° for ½ hr.	170° for ½ hr.	183-85° for ½ hr.
Biuret decomposed	78·5%	84·7%	88·0%
Phenylbiuret	11·1	10·3	9·5
Diphenylurea	36·5	40·1	45·1

The results are expressed in proportion to the respective theoretical yields.

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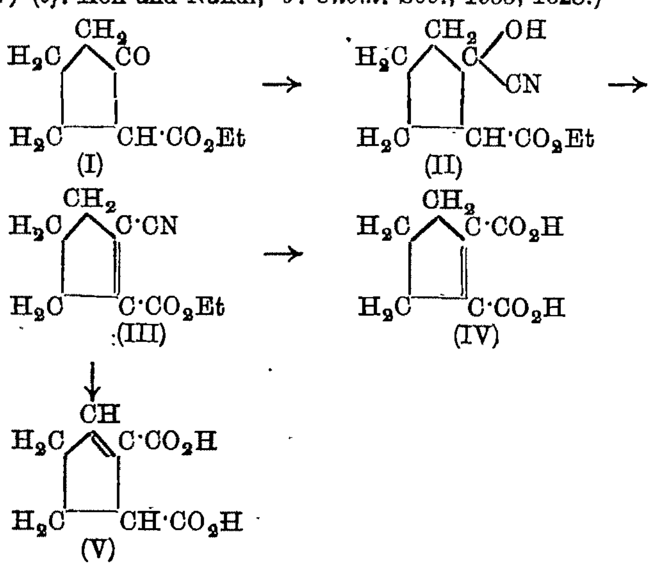
Synthesis of Δ^1 and Δ^2-*cyclo*Pentene-1 .2-dicarboxylic Acids

By Birendra Lal Nandi.

*cyclo*Pentene-1:2-dicarboxylic acid (IV) was first prepared by Hawarth and Perkin (*J. Chem. Soc.*, 1894, **65**, 978) from saturated *cyclo*pentane acid. Willstätter prepared the same acid (*Ber.*, 1895, **26**, 663) by cyclising ethyl $\alpha\alpha'$-dibromopimelate by means of sodium ethoxide and then hydrolysing the resultant cyclic unsaturated ester. Both the authors recorded the m.p. of the acid as 178° and they could not trace the presence of any isomeric acid. Hassell and Ingold, (*J. Chem. Soc.*, 1926, 1465) however, during the formation of ring compounds from straight chain bromo acids, isolated two isomeric *cyclo*pentene-1:2-dicarboxylic acids, m.p. 178° and 146° respectively from cyclisation of ethyl $\alpha\alpha'$-dibromopimelate. The present author, while studying the tautomeric capacity of unsaturated cyclic dicarboxylic acids under various conditions, found that both Perkin and Willstatter's methods gave rise to two isomeric acids namely the Δ^1- and Δ^2-*cyclo*pentene-1:2-dicarboxylic acids.

A rational synthesis of both the acids has been acomplished. Ethyl *cylco*pentane-1-one-2-carboxylate (I) obtained by cyclising ethyl adipate was converted into the nitrile (II) by means of HCN which on dehydration with thionyl chloride and pyridine gave the unsaturated cyano-ester (III). The latter, on alkaline hydrolysis, gave rise to a mixture of Δ^1-and Δ^2-*cyclo*pentene-1:2-dicarboxylic acids (IV) and (V) (*cf.* Kon and Nandi, *J. Chem. Soc.*, 1933, 1628.)



The constitution of the two isomeric acids has been confirmed by ozonisation. The ozonised product of ethyl ester of $\triangle^1$-acid gave diphenylhydrazone of ethyl $\alpha\alpha'$-diketopimelate, m.p. 147° (Blaise and Gault, *Bull. Soc. Chim.*, 1862, *i*, 4, 81). The ozonised product of the $\triangle^2$-acid, after decomposition of the ozonide and subsequent treatment with hydrogen peroxide, gave glutaric acid.

The two isomeric unsaturated acids were isolated by fractional crystallisation from ethyl acetate and water, the $\triangle^1$-acid separating first. Both the acids on equilibrations under standard conditions of Linstead and May (*J. Chem. Soc.*, 1927, 353, 362) gave rise to a mixture of the two isomeric acids of indefinite melting point. Unfortunately it was impossible to follow the interconversion because iodometric and bromometric methods of estimations of the two isomerides failed, since they had almost equal bromine additions (70% and 74% respectively) and iodine did not react with them at all. The barium and other suitable inorganic salt methods (Kon and Watson, *J. Chem. Soc.*, 1932, 2439) also failed since the barium, cadmium salts, etc., of both the isomeric acids are soluble in water.

EXPERIMENTAL.

Ethyl *cyclo*pentane 1-one-2-carboxylate was prepared by cyclising ethyl adipate (284 g.) in presence of molecular sodium (35 g.) in benzene, yield 80 %; b. p. 106-109°/12 mm.

Ethyl cyclo*pentane-1-hydroxy-1-cyano-2-carboxylate.*—To the above keto-ester (90 g.) was added potassium cyanide (100 g., 95% s.s.) in 20 % solution. The flask was fitted with a dropping funnel and a leadway for hydrocyanic acid. To the ice-cold solution was run in strong hydrochloric acid (200 c.c.) drop by drop with constant shaking (1 hour) and the whole left overnight at room temperature. The ester was extracted with ether, the ethereal solution washed once with dilute sodium carbonate solution, then with water, dried and the ether removed.

The residue was distilled with a drop of concentrated sulphuric acid, b.p. 143°/10 mm., yield 85%. (Found: C, 58·9; H, 7·0; N, 7·58. $C_9H_{13}O_3N$ requires C, 59·0; H, 7·1; N, 7·6 per cent).

Ethyl cyclo*pentene-1-cyano-2-carboxylate.*—Attempts were made to dehydrate the above cyanhydrin with different dehydrating agents and thionyl chloride in presence of pyridine was found to be the best. The cyanhydrin (74 g.) was mixed with pyridine (56 g.) and cooled in a freezing mixture. Thionyl chloride (40 g.) was added with

constant shaking in the course of half an hour and the flask was kept in the freezing mixture for another 2 hours and then at room temperature for 6 hours. Ice-cold water was added and the liquid extracted with ether; the ethereal solution was washed thoroughly with caustic soda solution (10%) till it was decolourised; it was washed with dilute hydrochloric acid, water, then dried and the ether removed. The unsaturated ester distilled at 132°/11 mm., yield 41 %. (Found: C, 65·8; H, 6·6; N, 8·8. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·7; N, 8·5 per cent).

$\triangle^1$- and $\triangle^2$-cyclo*Pentene-1:2-dicarboxylic acids.*—Ethyl *cyclo*-pentene-1-cyano-2-carboxylate (8 g.) was hydrolysed with 22% caustic potash solution (10 g.) under a condenser sufficiently short to permit the escape of alcohol vapour. After acidification the mixed isomeric acids were extracted with ether in a continuous extractor, m.p. 140-50°, yield 7·4 g. By repeated crystallisation of this impure acid from water 2·1 g. of $\triangle^1$-*cyclo*pentene-1:2-dicarboxylic acid were isolated, m.p. and mixed m.p. with Perkin's acid 178°. (Found: C, 53·8; H, 5·0. $C_7H_8O_4$ requires C, 53·9; H, 5·1 per cent).

The mother liquor was evaporated to dryness on a water-bath and the isomeric acid was purified by alternate crystallisation from water and ethyl acetate, m.p. 146°. (Found: C, 53·7; H, 5·0 per cent).

Oxidation of ethyl $\triangle^1$-cyclo*pentene-1:2-dicarboxylate.*—The pure $\triangle^1$- acid was esterified *via* silver salt, b.p. 140°/16 mm. d_4^{20}, 1 0805; n_D^{20}, 1·4652; $(R_L)D$, 54·26. (Found: C, 62·3; H, 7·8. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5 per cent).

The pure ester (7 g.) was dissolved in chloroform (100 c.c.) and a current of ozone was passed till absorption was complete (20 hrs.). After removal of the solvent at reduced pressure and decomposition of the ozonide by shaking with water (12 hrs.) and extracting with ether the residue gave the phenylhydrazone of ethyl $\alpha\alpha'$-diketo adipate from acetone melting at 147°. (Found: C, 64·9; H, 6·6. $C_{23}H_{28}O_4N_4$ requires C, 65·1; H, 6·6 per cent). That the oxidation product was ethyl $\alpha\alpha'$-diketo adipate was further proved by hydrolysis and subsequent oxidation by hydrogen peroxide to glutaric acid (m.p. and mixed m.p. with glutaric acid 97°).

Oxidation of $\triangle^2$-cyclo*pentene-1:2-dicarboxylic acid.*—The pure $\triangle^2$-acid (5 g.) was dissolved in dilute sodium carbonate solution (a little over theoretical) and a rapid stream of ozone was passed into it till absorption was complete (8 hrs.). After decomposition of the

ozonide by shaking, the product was extracted with ether after acidification. The residue after removal of ether did not give any phenylhydrazone. It was next dissolved in dilute caustic potash solution and treated with hydrogen peroxide (10 vol, 20 c.c.) and left overnight, acidified and again extracted with ether in a continuous extractor. 4·4 G. of a solid was isolated which when crystallised twice from ethyl acetate gave m.p. and mixed m.p. with glutaric acid, 97°.

Equilibrations.—Both the pure isomeric *cyclo*pentene-1:2-dicarboxylic acids (1 g.) were dissolved in the required amount (11 equivalents of a 25% solution by wt.) of caustic potash solution and heated for one hour in a closed tube in boiling water. After cooling the product was acidified with 19% hydrochloric acid and extracted with ether in a continuous extractor. In both the cases a mixture of acids was obtained melting indefinitely at 140-50° from which both Δ^1-and Δ^2-acids were separated by alternate crystallisation from ethyl acetate and water as stated above.

Under standard conditions of Linstead and May (*loc. cit.*) both Δ^1-acid and its isomeride gave almost instantaneous bromine additions (70% and 74% respectively of the theoretical amount in 10 minutes), while iodine did not react with them at all.

The barium, calcium, strontium and cadmium salts of both the isomeric acids are soluble in water.

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A Study of the Constitution of the Reduction Products of Chloral and Bromal Amides.

By B. H. Yelburgi and T. S. Wheeler.

The reduction of the group $CHOH{\cdot}CCl_3$ was studied by Jocitsch and co workers (*J. Russ. Chem. Soc.*, 1898, **30**, 920, 998) and Meldrum and Alimchandani (*J. Indian Chem. Soc.*, 1925, **2**, 1).

Using zinc shavings and boiling alcohol the former authors found that the reaction proceeded thus:

$$C_6H_5CHOH{\cdot}CCl_3 \longrightarrow C_6H_5CH{:}CCl_2 \longrightarrow C_6H_5CH{:}CH_2$$

Using zinc dust and glacial acetic acid the latter two authors concluded that the reduction gives $CH_2{\cdot}CHCl_2$.

The present research involves a study of the action of bromine, dry hydrogen chloride and dry hydrogen bromide on the reduction products of chloral benzamide, chloral acetamide, chloral propionamide* and bromal benzamide. The results indicate that with these compounds the group $CHOH{\cdot}CCl_3$ or $CHOH{\cdot}CBr_3$ is reduced to $CH{:}CCl_2$ or $CH{:}CBr_2$ under the conditions employed by Meldrum and Alimchandani (*loc. cit.*)

Action of bromine.—By mixing molecular quantities of the reduction product of chloral benzamide (4·72 g.) and bromine (3·5 g.) and hydrolysing the resulting compound by shaking it with water, the presence of the double bond was confirmed by the yield which was 6·6 g. (theoretical for addition 6·9 g.) If substitution had occurred the theoretical yield would have been 8·45 g. since half the bromine is eliminated as hydrogen bromide. The mechanism is as follows.

$$\underset{\text{(I)}}{R{\cdot}CO{\cdot}NH{\cdot}CHOH{\cdot}CCl_3} \xrightarrow{\text{reduction}} \underset{\text{(II)}}{R{\cdot}CO{\cdot}NH{\cdot}CH{:}CCl_2}$$

$$\xrightarrow{Br_2} \underset{\text{(unstable)}}{R{\cdot}CO{\cdot}NH{\cdot}CHBr{\cdot}C{<}^{Br}_{Cl_2}} \xrightarrow{HOH} RCO{\cdot}NH{\cdot}CHOH{\cdot}C{<}^{Br}_{Cl_2}$$

* These three reduction products were first prepared in these laboratories by Meldrum and Bhojraj (*Proceedings of the Indian Science Congress*, 1926, p. 146) by the action of zinc and acetic acid on the parent compounds. Editor.

Action of HCl *and* HBr.—The action was tried on the above mentioned four reduction products in dry ethereal solution and the work confirms the unsaturated formula for them. The mechanism is explained as follows,

$$\text{II} \xrightarrow[\text{addition}]{\text{HCl}} \underset{\substack{\text{(unstable)}\\ \text{(III)}}}{RCO{\cdot}NH{\cdot}CHCl_2} \xrightarrow{\text{HOH}} \underset{\text{(IV)}}{RCO{\cdot}NH{\cdot}CHOHCl_2}$$

The presence of the OH group in (IV) was confirmed by a number of reactions.

The chloral benzamide derivative has been studied in details.

(*i*) By the action of phosphorus pentachloride on (IV) an unstable chloro compound was obtained which was found to be identical with the unstable compound obtained by the action of hydrogen chloride on (II). This compound, not being stable, was transformed into an anilino derivative. The mechanism is as follows.

$$\begin{array}{ccccc} \text{(II)} & \xrightarrow{\text{HCl}} & \text{(III)} & \underset{PCl_5}{\overset{\text{HOH}}{\rightleftharpoons}} & \text{(IV)} \\ & & \downarrow{\scriptstyle C_6H_5NH_2} & & \\ & & C_6H_5CO{\cdot}NH{\cdot}\underset{\displaystyle |\atop HN{\cdot}C_6H_5}{CH}{\cdot}CHCl_2 & & \end{array}$$

(*ii*) The reactions of phosphorus pentabromide are similar to those of phosphorus pentachloride.

(*iii*) *Threefold action of acetic anhydride.*—IV, with acetic anhydride in the hot, in presence of concentrated sulphuric acid gives (II) and in cold it forms the acetyl derivative $C_6H_5CO{\cdot}NHCH\,(OAc){\cdot}CHCl_2$; in the cold in presence of alkali, it gives the anhydro derivative

$$\begin{array}{l} C_6H_5CO{\cdot}NH{\cdot}CH{\cdot}CHCl_2 \\ \qquad\qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad\qquad O \qquad \text{(V)} \\ \qquad\qquad\qquad\quad \diagup \\ C_6H_5CO{\cdot}NH{\cdot}CH{\cdot}CHCl_2 \end{array}$$

(*iv*) By the action of phosphorus pentoxide, (IV) gives (II).

(*v*) *Twofold action of benzoyl chloride.*—In the hot, in the presence of pyridine, IV gives V ; but in the cold, the benzoyl derivative is formed.

(*vi*) By the action of demethylsulphate, the methoxy derivative is formed.

The action of hydrogen chloride on the reduction products of chloral acetamide and chloral propionamide under similar conditions to the above, gave similar results. The yields are not good, ammonium chloride being also formed.

The action of hydrogen chloride or hydrogen bromide on β-dibromoethylene benzamide, prepared by reducing the acetyl derivative of bromal benzamide with zinc dust and glacial acetic acid, also yielded the expected results.

The presence of the OH group in the compound β-dibromo-α-hydroxyethyl benzamide was confirmed by preparing the acetyl, the anhydro and the methoxy derivatives by treating the compound with acetic anhydride and dimethylsulphate respectively.

With acetic anhydride in the cold, in presence of alkali the anhydro compound and the unsaturated compound are formed simultaneously.

$$\begin{array}{l} C_6H_5CO{\cdot}NH{\cdot}CH{\cdot}CHBr_2 \\ \qquad\qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad\qquad O \qquad \text{and } C_6H_4CO{\cdot}NH{\cdot}CH{:}CBr_2 \\ \qquad\qquad\qquad\quad \diagup \\ C_6H_5CO{\cdot}NH{\cdot}CH{\cdot}CHBr_2 \end{array}$$

The proof of the presence of the double bond in the reduction products is further confirmed by hydrogen analysis.

It should be noted that the present work refers to amides only and that the saturated formula may be true in other cases.

Experimental.

β-Dichloro-β-bromo-α-hydroxyethylbenzamide.—A dry chloroform solution of bromine (3·5 g.) was slowly added to chloroform solution of β-dichloroethylene benzamide (4·72 g.). Bromine was absorbed very quickly in the beginning. The resulting product was hydrolysed by shaking the mixture with water and then crystallised from dilute alcohol, m.p. 128-130°, yield 6·6 g. (Theoretical 6·9 g.). ($C_7H_8O_2NBrCl_2$ requires Halogen, 48·2. Found: Halogen, 48·0 per cent).

β-Dichloro-α-hydroxyethylbenzamide.—A dry ethereal solution of β-dichloroethylene benzamide (10 g.) was saturated with dry

HCl or dry HBr and kept under seal for a week. The viscous mass, obtained on evaporating ether, gave a crystalline solid on treatment with sodium carbonate solution, rhombic plates from chloroform and petroleum ether, m.p. 118-19°, yield 10 g. [Found: C, 46·4; H, 4·0; N, 6·0; Cl, 30·1; Mol. wt. (by Rast's camphor method) 238. $C_9H_9O_2NCl_2$ requires C, 46·2; H, 3·9; N, 6·0; Cl, 30·3 per cent; Mol. wt. 224].

β-Dichloro-α-chloroethylbenzamide.—The above compound (2 g.), was heated with phosphorus pentachloride (1·85 g.) and the product obtained after the removal of phosphorus oxychloride under reduced pressure was crystallised from dry ether as plates, m.p. 102-03°. The analytical results were unsatisfactory owing to the instability of the compound.

The identical compound was obtained after saturating the ethereal solution of β-dichloroethylene benzamide with dry HCl and keeping it sealed for a week, the ether was sucked off by means of a pump and the product was washed with ether three or four times and crystallised twice from dry ether in a vacuum desiccator, plates from dry ether, m.p. 102-03°, mixed m.p. with the product obtained using PCl_5, 102-03°. (Found: Cl, 42·0; $C_9H_8ONCl_3$ requires Cl, 42·2 per cent).

β-Dichloro-α-anilinoethylbenzamide.—The above chloro compound was treated with aniline (1 mol.) in presence of dimethylaniline (2·5 mols.) at 0° and the resulting anilino compound which separated was crystallised from chloroform and petroleum ether as needles, m.p. 190-92°. (Found: Cl, 22·8; $C_{15}H_{14}ON_2Cl_2$ requires Cl, 22·9 per cent).

β-Dichloro-α-bromoethylbenzamide.— β- Dichloro- α- hydroxyethyl benzamide (6 g.) and phosphorus pentabromide (11·1 g.) were heated and the resulting mixture was distilled at 155-220°/25 mm. This product was redistilled and collected at 168°/8 mm. ($C_9H_8ONBrCl_2$ requires Halogen, 50·3. Found: Halogen, 50·9 per cent).

This product was also obtained by passing dry HBr through the ethereal solution of β-dichloroethylene benzamide and distilling the mixture under reduced pressure. ($C_9H_8ONBrCl_2$ requires Halogen, 50·3. Found: Halogen, 51·0 per cent).

Action of Acetic Anhydride on β-Dichloro-α-hydroxyethylbenzamide.

(a) *β-Dichloroethylenebenzamide.* — β-Dichloro-α-hydroxyethyl benzamide (2 g.) was refluxed for 4 hours with acetic anhydride

(in excess) mixed with concentrated sulphuric acid. The resulting product was crystallised from dilute alcohol as needles, m.p. 68-9°. Mixed m.p. with identical sample shewed no depression.

(b) *β-Dichloro-α-acetylethylbenzamide.*—The reaction was carried out in the usual way at 0° (or in presence of pyridine in the cold) and the acetyl derivative after purification was crystallised from a mixture of ether and petroleum ether as needles, m.p. 146—48°. (Found: Cl, 25·7. $C_{11}H_{11}O_3NCl_2$ requires Cl, 25·7 per cent).

(c) *The anhydro compound of β-dichloro-α-hydroxyethylbenzamide.*—β-Dichloro-α-hydroxyethylbenzamide (2 g.) was dissolved in sodium hydroxide (100 c. c. 2 %) at 0° and acetic anhydride (0·9 g.) was at once added to it. The mixture must remain alkaline. (*cf.* Chattaway, *J. Chem. Soc.*, 1931, 2495). The resulting product was crystallised from dilute alcohol as needles, m.p. 189—90°. (Found: Cl, 31·3. $C_{18}H_{16}O_3N_2Cl_4$ requires Cl, 31·5 per cent).

The same compound can be obtained by heating β-dichloro-α-hydroxyethylbenzamide between 90-100° for about 6 hours.

A benzene solution of β-dichloro-α-hydroxyethylbenzamide was mixed with phosphorus pentoxide and refluxed on the water-bath for about 7 hours. The resulting product was identified as β-dichloroethylenebenzamide by means of the mixed melting point.

Action of Benzoyl Chloride on β-Dichloro-α-hydroxyethylbenzamide.

(*a*) *Anhydro derivative.*—The reaction with benzoyl chloride was carried out in the usual way and the resulting product was found to be the anhydro derivative, m.p. 189-90°. (Found: Cl, 31·3. $C_{18}H_{16}O_3N_2Cl_4$ requires Cl, 31·5 per cent).

(b) *β-Dichloro-α-benzoylethylbenzamide.*—2 G. of the substance were dissolved in pyridine at 0° and benzoyl chloride (1·5 g.) was slowly added. The mixture was well shaken and kept in the refrigerator for about 4 hours. Needles from dilute alcohol, m.p. 131°. (Found: Cl, 20·8. $C_{16}H_{13}O_3NCl_2$ requires Cl, 21·0 per cent).

β-Dichloro-α-methoxyethylbenzamide.— β-Dichloro-α-hydroxyethylbenzamide (2 g.) was dissolved in 2 % sodium hydroxide solution at 0° and dimethyl sulphate (2 g.) was slowly added with shaking. The methyl ether was crystallised from a mixture of ether and petroleum ether as needles, m.p. 99—100°. (Found : Cl, 28·4. $C_{10}H_{11}O_2NCl_2$ requires Cl, 28·6 per cent).

To confirm the presence of the double bond in β-dichloroethylene benzamide it was analysed for carbon and hydrogen. The results agree better with the unsaturated formula. (Found: C, 49·8; H, 3·3. $C_9H_7ONCl_2$ requires C, 50·0; H, 3·27 per cent. $C_9H_9ONCl_2$ requires C, 49·5; H, 4·2 per cent).

β-Dichloro-α hydroxyethylacetamide.—The process is the same as that for the corresponding benzamide derivative but ammonium chloride separates on keeping the ethereal solution saturated with hydrogen chloride. It was filtered and the solid obtained from the filtrate after hydrolysis with sodium carbonate solution was crystallised from a mixture of chloroform and petroleum ether, rhombic plates, m. p. 118-19°. The yield was about 50% while with benzamide derivative it was about 93 %. (Found: N, 8·1 ; Cl, 41·3. $C_4H_7O_2NCl_2$ requires, N, 8·1; Cl, 41·2 per cent).

To confirm the presence of the double bond in the reduction product of chloral acetamide it was analysed for carbon and hydrogen. (Found: C, 31·1; H, 3·3. $C_4H_5ONCl_2$ requires C, 31·1; H, 3·3 per cent. $C_4H_7ONCl_2$ requires C, 30·8; H, 4·5 per cent).

β-Dichloro-α-hydroxyethylpropionamide.—The process is the same as that for the corresponding acetamide derivative,. Here also ammonium chloride separated. The resulting product was crystallised from a mixture of chloroform and petroleum ether, rhombic plates, m.p. 116°. (Found: N. 7·6; Cl, 38·0. $C_5H_9O_2NCl_2$ requires N, 7·5; Cl, 38·1 per cent).

In this case also, the reduction product of chloralpropionamide was analysed for carbon and hydrogen. (Found: C, 35·5; H, 4·3. $C_5H_7ONCl_2$ requires C, 35·7; H, 4·2 per cent. $C_5H_9ONCl_2$ requires C, 35·5; H, 5·3 per cent).

β-Dibromoethylene benzamide was prepared by reducing acetylbromal benzamide (20 g.) dissolved in glacial acetic acid (80 c.c.) with zinc dust (6 g.) which was added at intervals. The mixture was shaken for about 4 hours and then filtered. On diluting the filtrate the reduction product was obtained as long thin plates from dilute alcohol, m.p. 75°. (Found: Br, 52·6. $C_9H_7ONBr_2$ requires Br, 52·5 per cent).

To show that the substance is unsaturated, it was analysed for carbon and hydrogen. (Found: C, 35·3; H, 2·46. $C_9H_7ONBr_2$ requires C, 35·41; H, 2·31 per cent. $C_9H_9ONBr_2$ requires C, 35·18; H, 2·95 per cent).

β-Dibromo-α-hydroxyethylbenzamide.—The ethereal solution of β-dibromoethylenebenzamide (4·5 g.) was saturated with dry hydrogen chloride or dry hydrogen bromide and treated asefore (*cf.* action of HCl on chloral benzamide derivative). The product was crystallised from a mixture of chloroform and petroleum ether as plates, m.p. 130°, yield 2·5 g. [Found: Br, 49·8; Mol. wt. (by Rast's camphor method) 329·6. $C_9H_9O_2NBr_2$ requires Br, 49·53 per cent. Mol. wt. 323].

Anhydro compound of β-dibromo-α-hydroxyethylbenzamide.—β-Dibromo-α-hydroxyethylbenzamide (2 g.) was dissolved in dilute sodium hydroxide solution at 0° and acetic anhydride (0·7 g.) was added to it and the mixture after being well shaken was left in the refrigerator for 1 hour and then filtered. The solid was crystallised from dilute methyl alcohol, m.p. 162°. (Found: Br, 51·1. $C_{18}H_{16}O_3N_2Br_4$ requires Br, 51·0 per cent).

The filtrate on being left in the refrigerator for 2 days gave a product, m.p. 74°. This was identified as the original reduction product by the mixed melting point.

(b) *β-Dibromo-α-acetylethylbenzamide.*—By carrying out the reaction with acetic anhydride at 0° in the usual way, the acetyl derivative was obtained as needles from absolute alcohol, m.p. 138°. (Found: Br, 43·8. $C_{11}H_{11}O_3NBr_2$ requires Br, 43·8 per cent).

β-Dibromo-α-methoxyethylbenzamide. — β - Dibromo-α-hydroxyethylbenzamide (1·5 g.) was dissolved in a dilute solution of sodium hydroxide at 0° and dimethyl sulphate (4 g.) was slowly added to it with shaking. The methyl ether was extracted with ether and crystallised, m.p. 124-26°. (Found: Br, 47·4. $C_{10}H_{11}O_2NBr_2$ requires Br, 47·5 per cent).

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Resolution of Co-ordinated Inorganic Compounds into Optical Isomers. Part I. Resolution of Triethylenediamino-cadmium Chloride, Bromide, Iodide and Sulphate.

By Panchanan Neogi and Gopal Krishna Mukherjee.

Existing literature shows that though several complex ethylenediamine compounds of trivalent metals like Cr, Co, etc., have been successfully resolved into their optical isomers, all attempts at resolution of ethylenediamine complexes of divalent metals like Ni, Zn, Cd, etc., have all along met with failure, among which may be mentioned the attempts of Bucknall and Wardlaw (*J. Chem. Soc.*, 1928, 2789) who tried to resolve triethylenediamino-nickel chloride by means of *d*-camphor sulphonic acid, *d*-tartaric acid, etc. Tris-dipyridyl compounds of divalent metals have, however, been resolved into optical isomers. Werner (*Ber.*, 1912, **45**, 433) was able to resolve tris-dipyridyl-ferrous salts and recently Morgan and Burstall (*J. Chem. Soc.*, 1931, 2213) have successfully resolved tris-α-pipyridyl-nickel chloride into their optical isomers by means of *d*-and *l*-ammonium tartrates.

In this paper attempts have been made to resolve triethylenediamino-cadmium salts into optical isomers by means of *d*-tartaric acid, *d*-camphor sulphonic acid, *d*-bromocamphor sulphonic acid, and *d*-sodiocamphor nitronate, when success was achieved with the last reagent only. *d*-Sodiocamphor nitronate was used by Werner himself in the resolution of triethylenediamino complexes of trivalent metals like chromium (*Ber.*, 1912, **45**, 865) in cases where other reagents failed to resolve. It appears, however, that this reagent has not hitherto been used for the resolution of the complex salts of divalent metals.

The *d*-tartrate, *d*-camphor sulphonate, and *d*-bromocamphor sulphonate of the cadmium complex were prepared and fractionally crystallised, but in all these cases the different fractions were found to have the same specific rotation and on removing the active residues, the resulting cadmium salt was found to be inactive. *d*-Sodiocamphor nitronate was then made use of in a way similar to that of

Werner in the case of complex chromium compounds (*loc. cit.*); but in this case no precipitate of the active substance occurred even when concentrated solutions of both the substances were taken. So the solution containing triethylenediamino-cadmium chloride and *d*-sodiocamphor nitronate was slowly evaporated in vacuum, when *d*-triethylenediamino-cadmium camphor nitronate slowly crystallised out. Three crops of crystals were thus collected which differed widely in their rotatory powers. On removing the camphor nitronate residue from the first fraction by means of dilute hydrochloric acid, the solution of the chloride was found to remain *dextro*-rotatory. It however, very soon racemised and crystallisation in vacuum yielded a *racemic* compound. But if to a fairly concentrated solution of the active salt excess of acetone be added, a crystalline precipitate of the active cadmium salt was obtained. The active solid retained its activity longer than its solution. The composition of the active substance was the same as that of the *racemic* salt.

The *laevo* variety of the substance could not, however, be obtained from the later fractions.

Attempts were then made to obtain the *laevo* variety by means of nitrocamphor itself, which is a *laevo*-rotatory substance, but up till now all attempts in this direction have met with failure. Further work is being done to isolate the *laevo* variety.

These salts which possess water of crystallisation lost weight when subjected to desiccation over concentrated sulphuric acid in vacuum and this fact was taken advantage of in the determination of the water of crystallisation.

The cadmium was estimated as cadmium sulphate in a platinum basin.

Experimental.

Preparation of d-*triethylenediamino-cadmium tartrate.*—Triethylenediamino-cadmium chloride was prepared according to the method used by Werner and co-workers (*Z. anorg. Chem.*, 1899, 21, 201). A concentrated solution of triethylenediamino-cadmium chloride (4 g.) was triturated with silver tartrate (4 g.) (prepared from a concentrated solution of Rochelle salt by precipitation with concentrated silver nitrate solution, washing with water and drying in a desiccator covered with black paper). The residue of silver chloride was repeatedly extracted with hot water and the extract filtered and evaporated in vacuum. Various fractions of crystals were thus obtained and all on

further purification by crystallisation gave a constant nitrogen content. (Found: N, 17·2 ; Cd, 22·4; H_2O, 10·8; $[Cd(En)_3](C_4H_4O_6)$, 3 H_2O requires N, 17·0; Cd, 22·73; H_2O, 10·93 per cent).

Rotation of this substance was measured in a 2 dcm. tube ; after four crystallisations the values of $[\alpha]^{30°}_D$ for the the first and the last fractions were 18·75° and 18·70° respectively. The tartrate was converted to the corresponding chloride by means of barium chloride but in each case the resulting solution was inactive.

Preparation of d-*triethylenediamino-cadmium camphor sulphonate.*—Freshly prepared silver oxide, obtained from $AgNO_3$ solution by precipitation with caustic soda and washing the residue with distilled water till free from the alkali salts, was dissolved in a warm solution of *d*-camphor sulphonic acid in water till a solution, neutral to litmus, was obtained. To a solution of triethylenediamino-cadmium chloride (5 g.) in water, the solution of the silver salt thus prepared was added till on adding one drop more it caused no further precipitate. The solution was filtered, evaporated in vacuum and fractionally crystallised and the different fractions further purified by recrystallisation. None of these fractions contained any chlorine and each gave a constant nitrogen content. (Found: N, 11·1; Cd, 14·27; H_2O, 2·3. $[Cd(En)_3](C_{10}H_{15}O_4S)_2$, H_2O requires N, 10·88; Cd, 14·55; H_2O, 2·33 per cent).

Rotations of the different fractions were observed in a 2 dcm. tube. After four crystallisations the values of $[\alpha]^{30°}_D$ for all these fractions were +15·0°. On acidifying a concentrated solution of any of these fractions with dilute hydrochloric acid and adding excess of acetone, triethylenediamino-cadmium chloride was precipitated which was found to be quite inactive.

Preparation of d-*triethylenediamino-cadmium bromocamphor sulphonate.*—A solution of the silver salt of *d*-bromocamphor sulphonic acid was prepared in the same way as the silver salt of *d*-camphor sulphonic acid by dissolving silver oxide in a warm solution of *d*-bromocamphor sulphonic acid till a solution neutral to litmus was obtained. To a solution of triethylenediamino-cadmium chloride (5 g.) in water, the silver bromocamphor sulphonate solution thus prepared was added till the addition of one drop more caused no further precipitate. The solution was filtered and the residue of silver chloride washed with water and the filtrate evaporated and fractionally crystallised and the different fractions purified by further crystallisation. None of these fractions was found to

to contain any chlorine and each gave the same nitrogen content. (Found: N, 8·5; Cd, 11·03; H_2O, 9·15. $[Cd(En)_3](C_{10}H_{14}BrSO_4)_2$, $5H_2O$ requires N, 8·38; Cd, 11·21; H_2O, 8·98 per cent).

Rotations of the different fractions were observed in a 2 dcm. tube. Each of the four fractions showed the value of $[\alpha]_D^{30}$ to be +138·0° On acidifying a concentrated solution of any of these fractions in water with hydrochloric acid and adding acetone in excess, the complex cadmium chloride was precipitated which was found to be quite inactive.

Preparation of d-triethylenediamino-cadmium camphor nitronate.—To a solution of triethylenediamino-cadmium chloride (4 g.) in water (10 c.c.) was added *d*-sodiocamphor nitronate (4·5 g.) dissolved in 15 c.c. of water and the mixture well shaken. No precipitate appeared. The solution was then subjected to fractional crystallisation in vacuum. The first fraction was recrystallised from water as very light yellow needles. This was completely free from chlorine. (Found: N, 15·7; Cd, 15·3; H_2O, 4·89. $[Cd(En)_3](C_{10}H_{14}O_3N)_2$, $2H_2O$ requires N, 15·65; Cd, 15·6; H_2O, 5·0 per cent).

Rotation of this substance was observed in a 2 dcm. tube with a 5% solution and the value of the $[\alpha]_D^{30}$ was found to be +133·2°. The second and the third fractions on further purification by crystallisation were found to have identical chemical composition and their specific rotations were +97·4° and +94·7° respectively under identical conditions.

d-Triethyelenediamino-cadmium chloride.—*d*-Triethylenediamino-cadmium camphor nitronate (first fraction) (2 g.) was dissolved in the least quantity of water and to the clear yellowish solution moderately dilute hydrochloric acid was added drop by drop and shaken till all the nitrocamphor had precipitated out and the solution became colourless which was then filtered and the residue washed with a small quantity of water. To the filtrate excess of acetone was added whereby a perfectly white crystalline substance was precipitated which was allowed to settle. The supernatant liquid was then decanted off and the precipitate washed several times with acetone to remove all traces of the acid and any free nitrocamphor. The residue was quickly dried underneath a fan between filter papers. (Found: N, 23·24; Cl, 19·45; Cd, 30·85. $[Cd(En)_3]Cl_2$ requires N, 23·15; Cl, 19·29; Cd, 30·79 per cent).

The substance (0·06 g.) was then dissolved in 15 c.c. of water and examined in a 2 dcm. tube when rotation was found to be +91°.

which makes $[\alpha]_D^{30}$, +113·7° and [M], +413·80°. The activity of the solution on being kept diminished rapidly and almost vanished in about an hour and a half. Examined after half an hour the specific rotation of the substance was found to be +51·28° under identical conditions. The solid, however, was found to be more stable when kept cool and examined after 3 hours, its specific rotation was fouud to be +12·5° under identical conditions, but when kept at the ordinary temperature (30°) it was found to be quite inactive after 2 hours.

d-*Triethylenediamino-cadmium bromide* was prepared in the same way as the chloride by decomposing the *d*-triethylenediamino-cadmium camphor nitronate (first fraction) with dilute hydrobromic acid and precipitation with acetone. (Found: N, 18·76; Br, 35·6; Cd, 24·49. $[Cd\ (En)_3]\ Br_2$ requires N, 18·59; Br, 35·42; Cd, 24·72 per cent).

Rotation of the substance (0·05 g. in 15 c.c. water) was determined in a 2 dcm. tube and was found to be +0·70° which makes the $[\alpha]_D^{30}$, +105·0° and [M], +474°. The solution completely racemised in 1 hour where as the solid, if kept cool was found to have a specific rotation of +7·5° after 3 hours, under identical conditions.

d-*Triethylenediamino-cadmium iodide* was prepared in the same way as the chloride by decomposing the *d*-triethylenediamino-cadmium camphor nitronate (first fraction) with hydroiodic acid, and precipitation with acetone. (Found: N, 15·56; I, 46·86; Cd, 20·26. $[Cd\ (En)_3]\ I_2$ requires N, 15·41; I, 46·48; Cd, 20·58 per cent).

Rotation of the substance was measured in a 2 dcm. tube with a solution of it (0·06 g.) in water (15 c.c.) and was found to be +0·72° which makes $[\alpha]_D^{30}$, +90° and [M], 491·4°. The iodide solution also racemised as readily as the bromide. The solid when kept cool and examined after 2 hours was found to be quite inactive.

d-*Triethylenediamino-cdmium sulphate* was also prepared in just the same way as the other salts by decomposing the *d*-triethylenediamino-cadmium camphor nitronate (first fraction)with dilute sulphuric acid and precipitation with acetone. (Found: N, 21·95; Cd, 29·12; SO_4, 24·30. $[Cd\ (En)_3]SO_4$ requires N, 21·65; Cd, 28·94; SO_4, 24·72 per cent).

Rotation of the substanee was determined in a 2 dcm. tube with a solution of it (0·12 g.) in water (15 c.c.) and was found

to be 1·33° which makes $[\alpha]_D^{30}$, $+83·1°$ and $+[M]$, 322°. The sulphate solution was found to be stabler than those described above as it retained its activity almost undiminished for half an hour but it also was found to be inactive when examined after 3 hours. The solid (kept cool) when examined after 3 hours was found to have a specific rotation of $+6·25°$ under identical conditions.

The corresponding active zinc salts were at first obtained in solution and have now been obtained in the solid condition. Further work on other salts is in progress.

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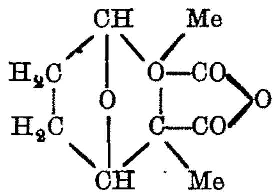
Attempts to Synthesise Cantharidin.*

By V. N. Pai and P. C. Guha.

According to the existing literature (Gadamer, *Arch. Pharm*, 1914, **252**, 624; 1916, **254**, 423; 1920, **258**, 171; Coffey, *Rec. trav. chim.*, 1923, **42**, 387, 1026) the most probable constitution of cantharidin is (I).



(I)

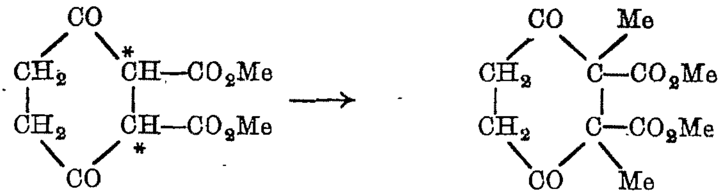
Although Bruchhausen and Bersch (*Arch. Pharm.*, 1928, **266**, 697) obtained dehydroprotocantharidin by condensing maleic anhydride with furan (*cf.* Diels, *Annalen*, 1927, **460**, 98) which on reduction gave protocantharidin, their attempt to synthesise dehydrocantharidin from furan and dimethylmaleic anhydride was not successful. Their interesting observation that cantharidin on being passed over palladised asbestos at 280° is decomposed into furan and dimethylmaleic anhydride confirmed definitely the constitution of cantharidin as (I).

Iyer and Guha (*J. Indian Inst. Sci.*, 1931, **14A**, 31) treated 1:2-dibromo-1:2-dimethyl*cyclo*hexane with an alcoholic solution of potassium cyanide to get the 1:2-dinitrile, the corresponding acid of which on anhydride formation was to give deoxycantharidin. Their attempts, however, were uusuccessful, only unworkable resinous mass being formed in every case.

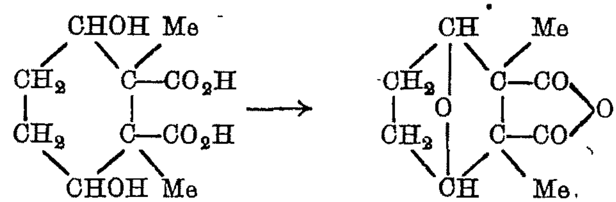
The next unsuccessful attempt to synthesise deoxycantharidin was made by Steele (*J. Amer. Chem. Soc.*, 1931, **53**, 283) who prepared $\alpha\alpha'$-dibromo-$\alpha\alpha'$-dimethylsuberic acid and attempted the elimination of the two bromine atoms with copper-bronze or molecular silver in order to obtain the anhydride of *cis*-1:2 dimethyl*cyclo*hexane-1:2-dicarboxylic acid.

An attempt has now been made to syhthesise cantharidin starting from methyl 3:6-diketo*cyclo*hexane-1:2-dicarboxylate (II) according to the following scheme:

* A preliminary report on this work has been published in the abstracts of papers, Chemistry section, *Indian Science Congress*, 1933, p. 18 and was communicated before the 15th October, 1932.



(II) (III)

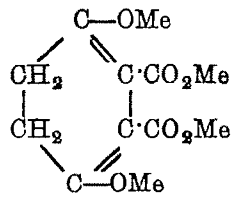


(IV) (I)

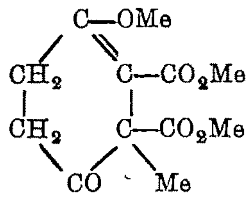
C-Dialkyl derivatives analogous to (III) have been prepared by Baeyer from succinosuccinic ester (*Ber.*, 1892, **25**, 2122; 1893, **26**, 232; Zelinsky and Naumow, *ibid.*, 1898, **31**, 3206).

From the disodium derivative of (II) and methyl iodide, Helferich (*Ber.*, 1921, **54**, 155) prepared methyl 2-methyl-3:6-diketo-*cyclo*hexane-1:2-dicarboxylate. In a second paper, Helferich and Bondenbender (*Ber.*, 1923, **56**, 1112) report that although the ester (II) contains two monoalkylated acetoacetic ester residues it does not give a di-*C*-methyl derivative and they do not give any experimental data. Since the method of attack outlined above for the synthesis of cantharidin seemed rather an attractive one, methylation has now been tried under varying conditions with a view to obtaining the desired *cis*-*C*-dimethyl compound.

The disodium derivative, however, reacts with methyl iodide when left in a closed bottle at the room temperature for 3 weeks to give a 60-70% yield of a neutral oil. Both analytical values and molecular weight agree with the formula $C_{12}H_{16}O_6$, but the substance does not give any semicarbazone or phenylhydrazone. Methoxyl determination by the Zeisel method, however, gives a value of 45·15%. The *C*-dimethyl derivative (III) should give a methoxyl value 24·22 % while the *O*-dimethyl compound (V) should give 48·44%. It would seem, therefore, that the product is the dimethyl ester contaminated possibly with some of the mono-*C*-methyl derivative (VI).



(V)



(VI)

The pure dimethyl ether has now been prepared by treating an alcoholic solution of the diketo diester (II) with dimethyl sulphate and aqueous alcoholic potassium hydroxide. When hydrolysed by means of an excess of aqueous alcoholic potash, the ring breaks up at the double bonds giving succinic acid as one of the products of decomposition; hydrolysis with boiling 10% sulphuric acid gives 1:4-diketo*cyclo*hexane. The ester slowly absorbs bromine in chloroform solution and decolorises an aqueous acetone solution of potassium permanganate. These facts show without doubt that the product is the methyl ester of 3:6-dimethoxy-4:5-dihydrophthalic acid (V).

The explanation for the anomaly, *viz.*, the formation of the dimethyl ether in this manner, and in such good yield and that of the mono-*C*-methyl derivative (Helferich, *loc. cit.*) is perhaps to be found in the difference of temperatures at which the reactions were carried out. The effect of temperature and solvent on the keto-enol equilibrium is well known (*cf.* Meyer, *Annalen*, 1911, **380**, 212; *Ber.*, 1911, **44**, 2718, 2799). An experiment in which the reaction mixture was kept in an ice-chamber for one month yielded only the mono-*C*-methyl compound.

An attempt to introduce a second methyl group through the potassium derivative of Helferich's mono-*C*-methyl compound has resulted in the formation of a *neutral* oil, which from methoxyl determination, appears to be a mixture of *C*-dimethyl (III) and *C*-methyl-*O*-methyl (VI) derivatives almost in equal quantities.

The diketo diester (II) with sodamide and methyl iodide (*cf.* Haller and Louvrier, *Compt. rend.*, 1914, **158**, 754, 1616; Ruzicka, *Ber.*, 1917, **50**, 1373; Baker, *J. Chem. Soc.*, 1931, 1651) in an atmosphere of nitrogen gave only the mono-*C*-methyl derivative. Treatment of the silver salt with methyl iodide has not been possible as the alcoholic solutions of the disodium salt of (II) and of silver nitrate gave immediately on mixing a black precipitate and mirror of metallic silver. The use of copper salt of methyl 2-methyl*cyclo*hexane-3:6-dione-1:2-dicarboxylate and methyl iodide (*cf.* Nef, *Annalen*, 1893, **276**, 200) has not been successful.

Renewed attempts to synthesise deoxycantharidin according to the scheme of Iyer and Guha (*loc. cit.*) were made according to the method of Rosenmund and Struck (*Ber.*, 1919, **52**, 1749) using cuprous cyanide as a catalyst with little success.

The synthesis of cantharidin is being tried starting from oxalyl diglycollic ester and succinyl dimethyldimalonic ester* results of which will form the subject of a subsequent communication.

Experimental.

Methyl 3:6-diketo*cyclo*hexane-1:2-dicarboxylate (II) was prepared according to Helferich's method (*loc. cit.*) *via* 2:3-dicyanohydroquinone and 3:6-dihydroxyphthalic acid with the following modifications.

2:3-*Dicyanohydroquinone.*—A three-necked flask (F) of 3-litre capacity (Fig. 1) is fitted with a mechanical stirrer (M), two separating funnels (S_1 and S_2), an exit tube (E) and a tube (T) to draw out the liquid. The tube (T) can be lowered into the flask when required. In the bell-jar (J) is placed a 2½-litre beaker containing crushed ice and the stopper of the bell-jar carries a tube connected with a water-jet pump. The whole apparatus is arranged in a fume cupboard fitted with a good exhaust fan.

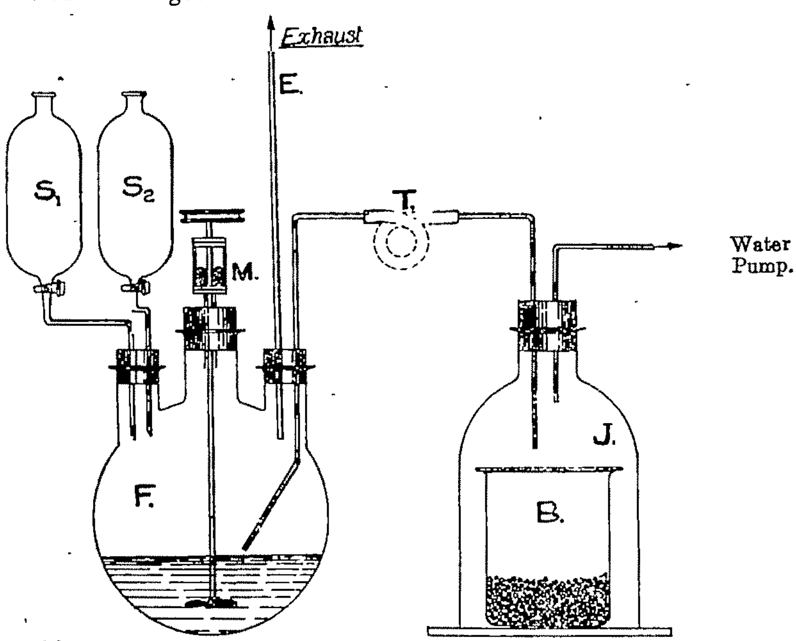


Fig. 1.

* This method is being worked out in collaboration with Mr. B. H. Iyer.

Powdered benzoquinone (33 g.) suspended in hot water (400 c.c., 80-90°) was taken in the flask and 5*N*-sulphuric acid (110 c.c.) added. The mechanical stirrer was then started vigorously, and from the separating funnel (S_1) was added a concentrated aqueous solution of 41 g. of pure sodium cyanide during 3 to 4 minutes. When the colour became deep green 5*N*-sulphuric acid (115 c.c.) was introduced from the funnel (S_2). The stirring was then stopped, the tube (T) lowered to the bottom of the flask, and the water-pump started, the solution rose in the tube and was discharged into the beaker containing about 2 lbs. of powdered ice. The solution deposited a brown solid (19 g.) which was crystallised from hot water (charcoal) as lustrous straw-yellow plates, charring at 230°. When left in a vaccuum desiccator over sulphuric acid, it loses its water of crystallisation and becomes almost white.

3:6-*Dihydroxyphthalic acid.*—The hydrolysis of the dinitrile was carried out essentially according to Helferich's method, except that smaller quantities of the nitrile (15 g.) and excess of potash (216 g.) were used in each experiment. It was found preferable to extract the acidified solution with ethyl acetate instead of ether.

Methylation of Methyl cyclo*Hexane*-3:6-*dione*-1:2-*dicarboxylate* (II).

(a) *With sodium methoxide in methyl alcohol and methyl iodide.*— The following is typical of many experiments carried out by this method. Methyl *cyclo*hexane-3:6-dione-1:2-dicarboxylate (6·8 g.) was taken in a round-bottomed flask (250 c.c.) fitted with a separating funnel, a condenser and inlet tube for passing nitrogen. The flask was first evacuated (3 mm.) by the Cenco pump and dry nitrogen passed slowly during the course of the reaction. To the clear solution obtained after the addition of absolute methyl alcohol (25 c.c.) was slowly added a solution of sodium (1·3 g.) in absolute methyl alcohol (35 c.c.). Methyl iodide (12 c.c.) was then introduced through the separating funnel to the clear dull yellow solution and the mixture heated under reflux on a water-bath for periods varying from 4 to 16 hours, fresh quantities of methyl iodide being added to make up for loss due to volatilisation. The residue after removal of alcohol and methyl iodide was acidified with 2*N*-sulphuric acid (25 c.c), extracted with ether, and the extract washed with 2*N*-potassium hydroxide solution until the alkali solution was no longer coloured. The deep-red alkaline extracts after acidification with

2*N*-sulphuric acid was extracted with ether which gave a red oily residue. The solid separating out of this oil in a vacuum desiccator on long standing crystallised from methyl alcohol in fine prisms, m. p. 91-93°, and was identified with 2-*C*-methyl derivative of Helferich.

(b) *With sodium methoxide and methyl iodide at room temperature.*—A mixture of the diketo diester (11·4 g.), sodium methoxide prepared from sodium (2·3 g.), methyl iodide (18 c.c.) and absolute methyl alcohol (70 c.c.) was left in a stoppered bottle at the room temperature for 3 weeks. From the neutral reaction product alcohol and methyl iodide were removed under reduced pressure, water added to the residue and the mixture extracted with ether. The faintly yellow viscous oil obtained from the extract distilled without decomposition at 140-44°/1 mm., yield 7 g. It did not give any coloration with ferric chloride. (Found: C, 56·14; H, 6·11; OMe, 45·15. $C_{12}H_{16}O_6$ requires C, 56·25; H, 6·25; OMe, 48·44 per cent).

(c) *With sodium hydroxide and dimethyl sulphate: Formation of the 3:6-dimethyl ether.*—To a solution of the diketo diester (10 g.) in methyl alcohol (20 c.c.) was added freshly distilled dimethyl sulphate (11·6 g.). To this mixture was poured slowly a solution of potassium hydroxide (2·6 g.) in water (5 c.c.) and alcohol (10 c.c.) with cooling. After removal of alcohol, the residue was treated with water and extracted with ether. The residue after removing the ether gave an oil distilling at 140-43°/1 mm. , yield about 38%. The oil slowly absorbs bromine in chloroform solution and decolorises an aqueous acetone solution of potassium permanganate and potassium carbonate. (Found: C, 56·35 ; H, 6·33 ; OMe, 48·19. $C_{12}H_{16}O_6$ requires C, 56·25 ; H, 6·25; OMe, 48·44 per cent).

(a) *Hydrolysis of Methyl 3:6-dimethoxy-4:5-dihydrophthalate* (V).—(*i*) *With sodium hydroxide.*—A mixture of the dimethoxy compound (4 g.) and an aqueous alcoholic solution of sodium hydroxide (6 g.) was kept for a day at the room temperature and then refluxed on the water-bath for 3 hours. The residue left after the removal of alcohol was acidified with 5*N*-sulphuric acid, the clear aqueous solution saturated with ammonium sulphate and then extracted with ether. The ethereal solution gave reddish oil from which a small quantity of a solid separated on standing in vacuum for 2 months. This melted at 179-80° and was identified as succinic acid by mixed m.p. with a genuine specimen (m.p. 180°).

(*ii*) *With sulphuric acid.*—The neutral ester (2 g.) mixed with concentrated sulphuric acid (8 c.c.) in 30 c.c. of water, was heated under reflux for 2 hours when the ester slowly went into solution with evolution of carbon dioxide. The solution was neutralised with sodium bicarbonate, saturated with ammonium sulphate and extracted four times with chloroform. The residue from chloroform crystallised from alcohol, m.p. 78°. The substance was identical with *cyclo*hexane-1 :4-dione obtained by hydrolysing (with 20% sulphuric acid) methyl *cyclo*hexane-2 :5--dione-1 :4-dicarboxylate.

Methylation of Helferich's mono-C-methyl compound.—The potassium salt of the mono-*C*-methyl compound was prepared at 0° by means of potassium methoxide in dry methyl alcohol, methyl iodide added, and the mixture kept in a closed bottle for a day. By working up the product in the usual manner, a viscous neutral oil was isolated which did not give any coloration with ferric chloride. Owing to the small quantity obtained so far, purification of this substance has not been accomplished yet, but as a preliminary to determining its nature, a methoxyl determination was made. The observed methoxyl value of 30·61 % is nearly the mean of the values for the *C*-dimethyl compound (III) (OMe, 24·22%) and the *C*-methyl-*O*-methyl derivative (VI) (OMe, 36·33%).

Interaction of potassium cyanide with 1 :2-*dibromo*-1 :2-*dimethyl*-cyclo*hexane.*—A mixture of the dibromo compound (2 5 g.), pure potassium cyanide (2 g.), water (6 c.c.) containing cuprous cyanide (0·6 g.) (prepared according to the method of Sudborough and James, "Practical Organic Chemistry", p. 202) and ethyl alcohol (3 c.c.) was heated in a Carius tube at 200° for 8 hours. The contents of the tube after removal of alcohol were acidified with hydrochloric acid, the ether extract of which left on evaporation a small quantity of a neutral gum which did not crystallise. The aqueous solution was distilled in steam and the distillate extracted with ether. The ether extract did not yield any definite product and the aqueous solution deposited a tarry residue on standing. The experiment was repeated several times using soda water bottles and heating for longer periods with no better results.

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Derivatives of Salicylic Acid. Part V. Synthesis and Constitution of 2-Nitrotoluene-6-sulphonic Acid. A Step towards the Synthesis of 6-Sulpho-salicylic Acid.

By Narhar Waman Hirwe and Mohiniram Rajaram Jambhekar.

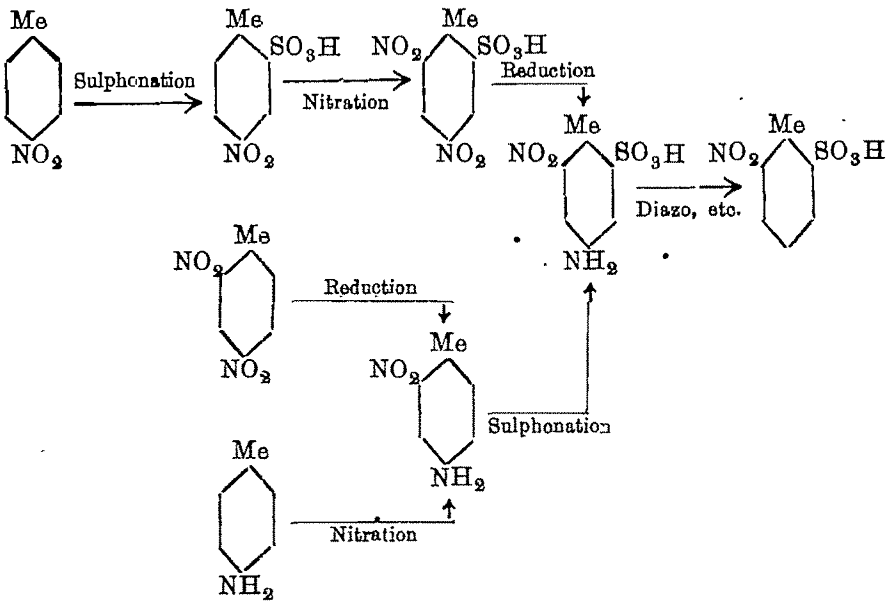
The object of the present investigation was to synthesise 6-sulpho-salicylic acid in the same way as the 4-sulpho-acid, worked out by us (*J. Indian Chem. Soc.*, 1933, **10**, 47). The present paper deals with the synthesis and constitution of the starting material, *viz.*, 2-nitro-toluene-6-sulphonic acid which has been obtained in the following way.

4-Nitrotoluene-6-sulphonic acid was prepared according to Jennsen (*Annalen*, 1874, **172**, 230). The yield of sulphonic acid increases considerably if the sulphonation mixture is kept exposed to atmosphere. It was further nitrated so as to obtain 2:4-dinitrotoluene-6-sulphonic acid. The dinitrotoluenesulphonic acid obtained by Beilstein and Kuhlberg (*Annalen*, 1870, **155**, 21), as shown by the composition of the lead salts, seems to be the same as that obtained later by Schanert (*Ber.*, 1877, **10**, 29) and is *o*-dinitrotoluene-*p*-sulphonic acid. Unlike the sulphochloride (m. p. 125°) obtained by the above authors, the sulphochloride (m.p. 107°) in the present paper did not give the sulphonamide being susceptible to the action of alkalies and ammonia.

The alcoholic ammonium sulphide solution selectively reduces the acid and its sulphochloride to give the 2-nitro-4-aminotoluene-6-sulphonic acid and 2-nitro-4-aminotoluene-6-sulphonamide respectively.

2-Nitrotoluene-6-sulphonic acid was then obtained from the above amino acid as usual *via* the diazo reaction.

That the 2-nitro-4-aminotoluene -6-sulphonic acid was produced by the partial reduction of 2:4-dinitrotoluene-6-sulphonic acid was supported by obtaining the same by the sulphonation of *o*-nitro-*p*-toluidine. *o*-Nitro-*p*-toluidine was obtained by partial reduction of 2:4-dinitrotoluene with sodium sulphide (Brand, *J. pr. Chem.*, 1906, *ii*, **74**, 470) and also by nitration of *p*-toluidine (Nölting and Collin, *Ber.*, 1884, **17**, 263).



It was found that 2:4-dinitrotoluene resisted all attempts at sulphonation. This is remarkable because the directing influences of the groups Me and NO_2 in 2 : 4-dinitrotoluene might be expected to lead to the introduction of the sulphonic acid group in the 6-position and remarkable also because the sulphonic acid in question (2:4-dinitrotoluene-6-sulphonic acid) is readily produced by the nitration of 4-nitro-6-sulphotoluene.

EXPERIMENTAL.

2:4-*Dinitrotoluene-6-sulphonic acid.* — *p*-Nitrotoluene-*o*-sulphonic acid (60 g.) (Jenssen, *loc. cit.*) was dissolved in sulphuric acid (120 g. *d* 1·82) and fuming nitric acid (28 g. *d* 1·51) was slowly added. The mixture was then heated on a water-bath for 3 hours and exposed to atmosphere when yellow crystals separated, m.p. 120°. The mixture was cooled, when a further yield of the crystals was obtained, yield 78 %. (Found: N, 9·28; S, 11·02; Equiv., 3.0·2 ; H_2O, 11·96. $C_7H_6O_7N_2S$, $2H_2O$ requires N, 9·39 ; S, 10·74 ; H_2O, 12·08 per cent. Equiv., 298).

Lead salt.—Yellow needles. [Found: Pb, 25·98 ; H_2O, 8·73. $(C_7H_5O_7N_2S)_2Pb$, $4H_2O$ requires Pb, 25·84 ; H_2O, 8·99 per cent].

Potassium salt was prepared by adding strong potassium chloride solution to that of acid. It is slightly soluble in cold water

and readily in hot water, from which it crystallised as tiny white plates. The anhydrous salt was obtained by heating it at 180° under reduced pressure for about 2 hours. (Found: K, 11·71 ; H_2O, 10·62. $C_7H_5O_7N_2SK$, $2H_2O$ requires K, 11·60 ; H_2O, 10·72 per cent).

Sodium salt is more soluble in water than potassium salt and crystallises in small anhydrous plates. (Found : Na, 7·87. $C_7H_5O_7N_2SNa$ requires Na, 8·09 per cent).

Calcium salt is highly soluble in water from which it crystallises in small microscopic needles with 4 mols. of water. [Found : Ca, 6·84 ; H_2O, 11·58. $(C_7H_5O_7N_2S)_2Ca$, $4H_2O$ requires Ca, 6·31 ; H_2O, 11·36 per cent].

Barium salt is easily soluble in cold water from which it crystallises in long glassy white needles with $4H_2O$. When heated to 180° under reduced pressure it becomes anhydrous. [Found : Ba, 18·72 ; H_2O, 9·68. $(C_7H_5O_7N_2S)_2Ba$, $4H_2O$ requires Ba, 18·74; H_2O, 9·85 per cent].

The *sulphonyl chloride*, prepared from the potassium salt and phosphorus pentachloride, crystallised from benzene in small plates, m.p. 107°. It is soluble in benzene and toluene and almost insoluble in alcohol and ether, yield 6·5 g. (Found: Cl, 12·88; S, 11·53. $C_7H_5O_6N_2ClS$ requires Cl, 12·66; S, 11·40 per cent).

2-*Nitro-4-aminotoluene-6-sulphonic acid.*—(*i*) 2:4-Dinitrotoluene-6-sulphonic acid (10 g.) was dissolved in alcohol (100 c.c,) and 5 *N*-ammonium sulphide (70 c.c.) and water (10 c.c.) were added and the mixture was refluxed on a water-bath for 2 hours, when sulphur precipitated which was filtered off. On concentrating the solution the amino acid was obtained on acidifying the solution of the ammonium salt. It is sparingly soluble in water from which it crystallises in small white needles, m.p. 270° (decomp.), yield 6·5 g. (Found: N, 11·91; S, 13·87. Equiv., 233·1. $C_7H_8O_5N_2S$ requires N, 12·06; S, 13·79; per cent. and Equiv., 232).

(*ii*) *o*-Nitro-*p*-toluidine (5 g.) (Brand, *loc. cit.*, Nölting and Collin *loc cit.*), was sulphonated by heating it on a water-bath with fuming sulphuric acid (20% SO_3) for 6 hours. On pouring the mixture in water white solid separated which was filtered and purified by dissolving in sodium carbonate solution and then precipitating with dilute hydrochloric acid. Decomposition temperature, analysis and derivatives agree with that of the above. The *potassium* salt crystallised from water in yellowish red stout rectangular plates.

(Found: K, 12·90; H_2O, 11·44. $C_7H_7O_5N_2SK$ requires K, 12·75; H_2O, 11 77 per cent).

The *sulphonyl chloride* was prepared from the potassium salt (10 g.) and phosphorus pentachloride (25 g.). It is soluble in benzene and toluene from which it crystallises in pale yellow needles, m.p. above 260° (decomp.), yield 7 g. (Found: Cl, 14·20; S, 12·72. $C_7H_7O_4N_2ClS$ requires Cl, 14·19; S, 12·77 per cent).

The *sulphonamide* was obtained from the chloride and ammonia (*d* 0·880). It is soluble in water from which it crystallises in yellow plates, m.p. 230°. (Found: N, 18·16; S, 13·85. $C_7H_9O_4N_3S$ requires N, 18·18; S, 13·86 per cent).

2-*Nitro-4-diazotoluene-6-sulphonate*.—2-Nitro-4-aminotoluene-6-sulphonic acid (15 g.) was diazotised at 0°. The solid separating was filtered and washed several times with cold water, yield 9 g. It is insoluble in water and explodes violently at 160° when heated slowly and at 164° when heated rapidly.

2-*Nitrotoluene-6-sulphonic acid*.—The above diazo compound was dissolved in alcohol and refluxed for 8 hours. On evaporating the mixture on a water-bath and then in desiccator a dark solid was obtained which is very hygroscopic. On drying this solid on a porous plate a yellow nonhygroscopic solid remains which was recrystallised from water as yellow cluster of needles, m.p. 127°. It gives dark coloured salts. (Found: N, 5·45; S, 12·57; H_2O, 14·08. $C_7H_7O_5$-NS, $2H_2O$ requires N, 5·53; S, 12·66; H_2O, 14·23 per cent).

The *barium salt* is easily soluble in water from which it crystallises in dark red needles. [Found: Ba, 19·11; H_2O, 19·86. $(C_7H_6$-$O_5NS)_2Ba$, $8H_2O$ requires Ba, 19·20; H_2O, 20·19 per cent].

The *sulphonamide* was obtained as usual by the action of ammonia on 2-nitrotoluene-6-sulphonyl chloride (liquid). It crystallised from water in white rectangular plates, m.p. 165°. (Found: S, 14·58; $C_7H_8O_4N_2S$ requires S, 14·83 per cent).

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On a New Method of Calculation of Vibration Frequencies of Atoms.

By Binayendra Nath Sen.

The frequency of vibration of atoms of elements has been the subject of investigation of several authors (Einstien, *Ann. Physik*, 1911, *iv*, **34**, 170; Lindemann, *Physikal. Z.*, 1910, **11**, 609; *Z. Elektrochem.*, 1911, **17**, 822; *Ber. Phys. Ges.*, 1911, **13**, 1107; Wagstaff, *Phil. Mag.*, 1924, *vi*, **47**, 84). Each author has given his own formula for computing the value of atomic frequencies, which although of great theoretical interest and of practical importance, does not always give values in close agreement with the experimental ones. It was, therefore, thought by the present author that one or more of the factors on which the atomic frequency depends has been lost sight of and it is the object of the present paper to discuss such factors and propose a formula for the determination of atomic frequencies of elements which would give results in close agreement with the experimental ones.

In the present formula certain assumptions have been made with respect to the constraint on the atom. The atomic spheres which are capable of vibration about their mean positions in an environment full of energy may be considered to be under a certain state of tension determined by the parachor of the element and the electrical field in the neighbourhood. The constraint may be assumed to be directly proportional to $\frac{P-V}{V}$ where P is the parachor and V, the atomic volume of the element, as also to Ze^2/r^3 where Z is the valency, e the elementary charge and r, the atomic radius.

Supposing the substance contains a system of atomic vibrators of frequency ν, then according to the simple theory of harmonic motion,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{p}{m}} \qquad (1)$$

where 'm' is the atomic mass and 'p' the constraint on the atom.

Assuming the constraint on the atom to be proportional to the factors already indicated, the equation (1) changes to

$$\nu = \frac{1}{2\pi} \cdot \sqrt{\frac{k.\frac{P-V}{V.} \cdot \frac{Ze^2}{r^3}}{m}}$$

We can finally have,

$$\nu = \sqrt{k}. \frac{1}{2\pi} \sqrt{\frac{P-V}{V}. \frac{Ze^2}{r^3}. \frac{N}{M}}$$

where $k = 0{\cdot}415 \times 10^{12}$, $N = 6{\cdot}06 \times 10^{23}$ (Avogadro's number) and M = the atomic weight of the element.

The physical and mathematical significance of the relation

$$p = k.\frac{P-V}{V}. \frac{Ze^2}{r^3}$$

will form the subject of another communication.

The values for parachors of elements have been taken from Sugden's "Parachor and Valency," p. 181.

As regards the atomic radii of the different elements, Bragg's values (Bragg, *Phil. Mag.*, 1920, *vi*, **40**, 169) have been throughout adopted in the calculations. In the absence of Bragg's value for the atomic diameter of mercury, Perrin's value (*Ann. chim. phys.*, 1909, *viii*, **18**, 5) has been taken as it has been confirmed by later work (*cf.* Henry, *Compt. rend.*, 1912, **154**, 880) ; Saha's value, as it would appear from his own statement (*Nature*, 1921, **170**, 682), is too small.

The values for the atomic volumes have been adopted from the tables used by Lewis (*J. Amer. Chem. Soc.*, 1907, **29**, 1165, 1516) and Wagstaff (*Phil. Mag.*, 1924, *vi*, **47**, 84).

The question of selection of valencies appears to present some difficulty in the case of elements with variable valencies. In these cases such valency is adopted as is exhibited in the direct formation of chlorides or bromides by the action of halogens or in the indirect formation of the stablest halides.

Mercury has thus been assumed to be divalent because the free metal directly unites with chlorine to form the dichloride (Cowper, *J. Chem. Soc.*, 1883, **43**, 153; Balard, *Ann. chim. phys.*, 1826, *ii*, **32**, 337). Slight traces of mercurous chloride are, however, formed

owing to the reducing action of the metal but the compound is unstable and is dissociated in the vaporous state (Harris and Meyer, *Ber.*, 1894, **27**, 1842).

Lead has been assumed to be divalent in as much as lead chloride is only formed by the direct action of chlorine on the metal (Weber, *Pogg. Ann.*, 1861 **112**, 659; Fischer, *J. Chem. Soc.*, 1879, **35**, 282).

Copper when heated in chlorine forms only the dichloride and is hence assumed to be divalent. Any trace of cuprous chloride formed, however, passes into the dichloride (Mellor, "Treatise on Inorganic Chemistry", Vol. III. p. 168).

Arsenic forms only the trichloride when the free element burns in chlorine gas (Dumas, *Ann. chim. phys.*, 1828, *ii*, **38**, 337; Rose, *Pogg. Ann.*, 1841, **52**, 62 ; Capitine, *J. Pharm. Chem.*, 1839, *iii*, **25**, 524). Also, the pentachloride is dissociated at an elevated temperature into arsenic trichloride and chlorine. These have led us to assume arsenic to be a trivalent element.

Nickel and chromium have been assumed to be di - and trivalent elements respectively as they exhibit these valencies in their stable chlorides.

In the case of other elements dealt with in this paper their usual valencies have been adopted.

In the following tables the observed values of frequencies are those calculated by Nernst and Lindemann's atomic heat formula (*Z. Elektrochem.*, 1911, **17**, 822), which represents experimental values with great exactitude.

TABLE I.

Element.	Parachor.	Atomic vol.	Atomic radius.	Valency.	Atomic wt.	ν cal.	ν obs.
Mercury	69·0	14·8	1·73	2	200·60	$2{\cdot}1 \times 10^{12}$	$2{\cdot}2 \times 10^{12}$
Lead	76·2	18·2	1·90	2	207·20	1·64	1·9
Iodine	91·0	25·7	1·40	1	126·92	2·1	2·0
Copper	46·0	7·10	1·37	2	63·57	6·35	6·6
Aluminium	38·6	10·1	1·35	3	27·10	8·7	8·3
Zinc	50·7	9·5	1·325	2	65·37	5·8	$4{\cdot}8 \times 10^{12}$

TABLE II.

Elements.	Parachor.	Atomic vol.	Atomic radius.	Valency.	Atomic wt.	ν cal.	ν obs.
Bromine	68·0	25·1	1·19	1	79·92	$2{\cdot}76 \times 10^{12}$	...
Silicon	25·0	11·4	1·175	4	28·30	9·96	...
Chlorine	54·3	25·0	1·05	1	35·46	4·14	...
Chromium	54·0	7·76	1·40	3	52·00	8·68	...
Nickel	50·0	6·67	1·35	2	58·68	7·36	...
Arsenic	50·1	13·3	1·26	3	74·96	5·76	...
Selenium	62·5	18·5	1·175	4	79·20	6·67	...
Sulphur	48·2	15·5	1·025	4	32·06	12·13	$7{\cdot}3 \times 10^{12}$

The values of frequencies calculated by the formula, agree well with those observed where such values are available and compare well with those obtained by Lindemann (*loc. cit.*), Wagstaff (*Phil. Mag.*, 1924, *vi*, **47**, 87), Debye (Allen, *Proc. Roy. Soc.*, 1917, **A**, **94**, 100), and other formulae as indicated in Table III.

TABLE III.

Elements.	Einstein's formula.	Wagstaff's formula.	Valencies as adopted by Author.	Valencies as adopted by Lindemann.*	Lindemann's formula based on photoelectric effect.	Debye formula.	Lindemann's m. p. formula.	Author's formula.	ν obs.
Mercury	$1{\cdot}46 \times 10^{12}$	$1{\cdot}9 \times 10^{12}$	2	1	$2{\cdot}0 \times 10^{12}$	...	$1{\cdot}3 \times 10^{12}$	$2{\cdot}1 \times 10^{12}$	$2{\cdot}2 \times 10^{12}$
Lead	2·2	1·55	2	2	2·5	$1{\cdot}49 \times 10^{12}$	1·84	1·64	1·9
Iodine	...	...	1	1	1·9	...	1·7	2·1	2·0
Copper	5·7	6·0	2	2	7·2	6·81	6·7	6·85	6·6
Aluminium	6·6	5·93 7·0	3	1	8·2	8·26	7·5	8·7	8·3
Zinc	3·73	3·9	2	...	...	...	4·36	5·8	4·8
Bromine	...	...	1	...	...	...	2·45	2·76	...
Silicon	...	...	4	...	...	...	9·6	9·96	...
Chlorine	...	...	1	...	...	...	3·68	4·14	...
Chromium	...	...	3	...	...	9·01	8·3	8·68	...
Sulphur	...	...	4	2	6·6	...	3·9	12·13	7·3
Nickel	6·6	8·27	2	...	...	...	8·2	7·36	...
Arsenic	...	...	3	...	...	...	4·36	5·76	...
Selenium	...	...	4	...	...	...	4·06 (Wagstaff, *loc. cit.*)	6·67	...

* These values of valencies have been adopted by Lindemann in his formula based on photoelectric effect (*Ber., Phys. Ges.*, 1911, 13, 1107).

2

SUMMARY.

A new formula has been proposed for the calculation of atomic frequencies from parachor, atomic volume, valency, Avogadro's number, atomic weight and the elementary charge, *viz.*,

$$\nu = \sqrt{k}.\ \frac{1}{2\pi}\ \sqrt{\frac{P-V}{V}.\ \frac{Ze^2}{r^3}.\ \frac{N}{M}}$$

which bears out values observed experimentally as well as those calculated by other formulae.

My thanks are due to Dr. P. Neogi and Prof. A. Maitra for their kind interest in the work.

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The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part III. The Bromination of Some μ-Substituted Benzthiazoles

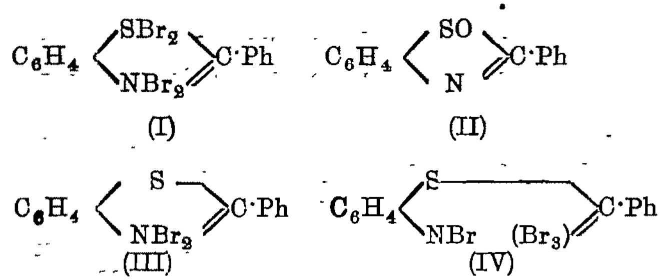
By Mahmud Ahmed Shahabuddin Chaudhri, Ranchhodji Dajibhai Desai and Robert Fergus Hunter.

One of the objects of this series of papers (Farooq and Hunter, *J. Indian Chem. Soc.*, 1932, **9**, 545) is to examine the effect of substituents on the formation and stability of the polybromide derivatives of heterocyclic compounds, and in this connexion it appeared desirable to re-examine more closely some of the bromo-addition compounds of 1-substituted benzthiazoles which were obtained in earlier investigations. The opportunity was also taken to extend our observations to the bromination of certain members of the group which have not received previous attention.

It was observed some years ago by one of us that treatment of a solution of 1-chlorobenzthiazole in chloroform with excess of bromine gives rise to a dibromo-addition product of the thiazole base (Hunter, *J. Chem. Soc.*, 1925, **127**, 1488). No particular precautions were paid, however, with regard to the exclusion of moisture from the reagents employed in the original experiment and we now find that the use of sodium-dried bromine and chloroform, which has been dried over phosphorus pentoxide in this and in other brominations desribed in this paper, has little or no effect on the formation of the bromo-addition compound. The dibromide of 1-chlorobenzthiazole in common with most benzthiazoles containing a free *o*- and *p*-position to the nuclear nitrogen atom, gives low values for labile bromine on iodometric titration under the usual conditions, although it regenerates the original chlorothiazole on treatment with sulphurous acid (*cf.* Hunter. *J. Chem. Soc.*, 1930, 138 ; Farooq and Hunter, *loc. cit.*).

Attention was next directed to the tetrabromide of 1-phenylbenzthiazole to which the formula (I) was assigned by Bogert and Abrahamson some eleven years ago (*J. Amer. Chem. Soc.*, 1922, **44**, 826). The fact that this compound does not yield a sulphoxide (II) on treatment with mercuric oxide (Hunter, *J. Chem. Soc.*, 1930, 126) and the

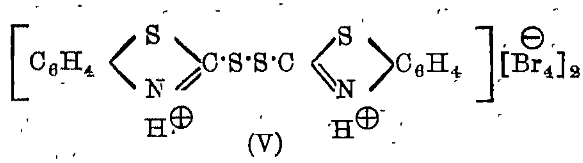
existence of the tetrabromides of pyridine (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558) and quinoline (Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124), however, clearly invalidate the thiazonium bromide structure and suggest that the tetrabromide probably has the formula (IV). If this is the case, it is clear that a dibromide (III), analogous to benzthiazole dibromide itself, should be the precursor of the tetrabromide obtained by bromination of 1-phenylbenzthiazole.



(I) (II) (III) (IV)

Actually a substance having the composition of a dibromide of the phenylthiazole is readily obtained in the presence of a lower concentration of the halogen. Both this substance and the tetrabromide give low values for labile bromine on iodometric titration, due to nuclear substitution under the conditions of the determination.

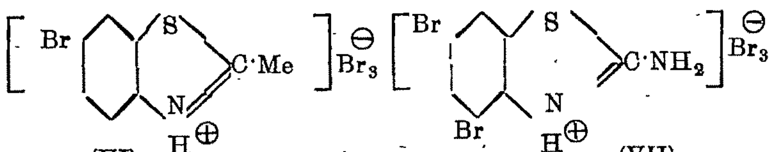
It has been shown in an earlier investigation that the bromination of 1-thiolbenzthiazole gives rise to a tetrabromo-addition compound which yields benzthiazolyl-1:1-disulphide on reduction with sulphurous acid. A re-examination of this tetrabromo derivative has shown that it is actually a dihydrotetrabromide of the disulphide (V); three of the four bromine atoms being labile towards hydroiodic acid. The initial action of bromine on 1-thiolbenzthiazole is clearly, therefore, one of oxidation, giving rise to a hydrobromic acid salt of the disulphide which then combines with bromine, yielding the dihydrotetrabromide (V).



(V)

The bromination of 1-methylbenzthiazole, which has not previously been examined, presented unusual difficulty. The ultimate product is a hydrotribromide of a monobromo-substitution derivative which is most probably the 5-bromo compound (VI), but its forma-

tion appears to be preceded by that of a true addition product of bromine with the unsubstituted methylbenzthiazole.

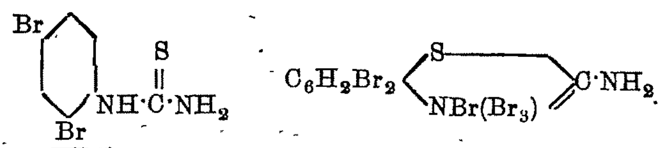


(VI) (VII)

This recalls the behaviour of 1-aminobenzthiazole which at low temperatures yields a labile dibromo-addition compound rapidly isomerising to the hydrobromide of 5-bromo-1-aminobenzthiazole (Hunter, *loc. cit.*), and it, therefore, appeared of interest to examine the effect of further bromination on 5-bromo-1-aminobenzthiazole.

At 0°, however, this base underwent nuclear substitution yielding a hydrotribromide of a dibromoaminobenzthiazole whose constitution (VII) follows from the synthesis of the dibromo base, obtained by reduction with sulphurous acid from 2:4-dibromophenylthiocarbimide by way of the thiocarbamide (VIII).

With substitution of hydrogen *ortho* to the nuclear nitrogen atom in 5-bromo-1-aminobenzthiazole by bromine, further halogen substitution is suppressed (*cf.* Dyson, Hunter, Jones, and Styles, *loc. cit.*) and bromination of 3:5-dibromo-1-aminobenzthiazole under the usual conditions gives rise to a tetrabromide (IX), which regenerates the dibromoaminobenzthiazole on treatment with sulphurous acid.



(VIII) (IX)

Experimental.

For the following experiments, sodium-dried bromine (B.D.H.) was used and the chloroform was first dried and thereafter redistilled over phosphorus pentoxide.

1-*Chlorobenzthiazole dibromide*, prepared by concentrating in a vacuum at laboratory temperature the solution obtained by treating the chlorothiazole (1 g.) in chloroform (5 c.c.) with bromine (1 c.c. in 1 c.c. of the same solvent), formed yellow crystals which had m.p. 182° after drying in a vacuum. [Found: Br (total), 48·5; Br (labile),

27·0. Calc. for $C_7H_4NClS(Br_2)$, Br (total and labile), 48·6 per cent]. It dissolved in sulphurous acid giving a colourless solution which on basification yielded 1-chlorobenzthiazole which was identified by its properties and by its conversion into 1-anilinobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126; 1880, **13**, 11), which had m. p. 158° alone and when mixed with an authentic specimen.

1-Phenylbenzthiazole, prepared by the thionation of benzanilide, was redistilled in *vacuo* and recrystallised from dilute alcohol when it formed long needles, m.p. 114° (Bogert and Abrahamson, *loc. cit.*).

1-*Phenylbenzthiazole dibromide*.—A solution of the base (2 g.) in chloroform (10 c.c.) was treated with bromine (0·6 c.c. in 0·6 c.c. of the same solvent) at 0°, and the mixture was kept in a freezing mixture when the dibromide separated in yellow needles, m.p. 119° after being dried in a vacuum. [Found: Br (total), 44·9; Br (labile), 30·9. $C_{13}H_9NS(Br_2)$ requires Br (total and labile), 43·1 per cent]. On treatment with sulphurous acid, the dibromide regenerated 1-phenylbenzthiazole which was identified by m.p. and mixed m.p. determination.

1-*Phenylbenzthiazole tetrabromide*.—A specimen of this compound, prepared as already described by one of us, showed the usual discrepancy between determinations for total and labile bromine (*J. Chem. Soc.*, 1930, 138). The decolorised chloroform layer obtained in iodometric titration was, therefore, separated, the solvent removed on a steam bath and the residue was recrystallised from alcohol. It had m.p. 98° and contained halogen, but it was not found possible to isolate 5-bromo-1-phenylbenzthiazole on account of the closeness of its solubility to that of 1-phenylbenzthiazole in ordinary solvents.

Thermal decomposition.—A freshly prepared specimen of the tetrabromide was heated in an oil-bath at 120° at 5 mm. pressure for 5 minutes, when the compound showed obvious signs of decomposition. The residue gave the following figures on analysis. [Found: Br (total), 42·2; Br (labile), 22·0 per cent], and yielded 1-phenylbenzthiazole unaccompanied by 5-bromo-1-phenylbenzthiazole on reduction with sulphurous acid.

1-Thiolbenzthiazole was prepared as follows:—A mixture of acetanilide (500 g.) and sulphur (300 g.) was heated in a pyrex flask at its b. p. for 58 hours and the sublimated 1:1-bis-benzthiazole (Hofmann, *Ber.*, 1880, **13**, 1223) was extracted with 60% sulphuric acid (Lauth, *Bull. Soc. chim.*, 1896, **15**, 82), isolated by precipitation with water and purified by sublimation. An intimate mixture of the

bisthiazole (10 g.) and powdered potassium hydroxide (20 g.) was heated in an oil-bath at 200° until complete fusion occurred. The mixture was cooled, treated with ice water (100 c.c.) and the alkaline solution of the sodium salt of *o*-aminophenylmercaptan was filtered through asbestos and neutralised with dilute hydrochloric acid. The mixture of *o*-aminophenylmercaptan and *o*-aminophenyldisulphide, so obtained, was extracted with ether and the product was reduced with zinc and concentrated hydrochloric acid in the usual way. A mixture of the zinc salt of *o*-aminophenylmercaptan (2 g.), carbon disulphide (4 c.c.) and alcohol (25 c.c.) was heated under reflux for 6 hours and the oil obtained after removal of the solvent and excess of carbon disulphide was acidified with dilute hydrochloric acid. On recrystallisation of the precipitated solid from alcohol, 1-thiolbenzthiazole was obtained in yellow needles, m.p. 179°.

Benzthiazolyl-1 : 1-*disulphide dihydrotetrabromide*.—A solution of the thiolbenzthiazole (1 g.) in chloroform was treated with bromine (1·5 c.c. in 1·5 c.c. of chloroform) at 0°. The bromo-addition compound formed orange plates which had m.p. 127° (decomp.) after drying. [Found: Br (total), 66·0; Br (labile), 40·6. $C_{14}H_8N_2S_4$, $2 \cdot HBr(Br_3)$ requires Br(total), 65·5; Br(labile), 49·0 per cent]. On reduction with sulphurous acid it yielded benzthiazolyl 1 : 1-disulphide, m.p. 180°. A mixture of the disulphide and the original thiolbenzthiazole melted at 159°.

Bromination of 1-*methylbenzthiazole*.—(*i*) 1G. of 1-methylbenzthiazole (Jacobson, *Ber*., 1886, **19**, 1069) in chloroform (5 c.c.) was treated with bromine (1 c.c. in 1 c.c. of chloroform) at 0°. As no separation of a bromo-addition product took place the solution was concentrated in a vacuum at laboratory temperature, when an orang-eyellow product was obtained, m.p. 76°. [Found: Br(total), 45·5; Br(labile), 27·2 per cent]. (*ii*) In a similar experiment in which the methylbenzthiazole (1 g. in 20 c.c. of chloroform) was treated with bromine (3 c.c. in 3 c.c. of chloroform), yellow plates were obtained, contaminated by a certain amount of gummy material which was removed by trituration with chloroform. The *hydrotribromide* of the bromomethylbenzthiazole obtained in this way melted at 70°. [Found: Br(total), 64·5; Br(labile), 33·9. C_8H_6NBrS, $HBr(Br_2)$ requires Br(total), 68·2; Br(labile), 34·1 per cent]. The hydrotribromide dissolved in sulphurous acid giving a colourless solution which on basification, extraction with ether and removal of the ether on a steam bath yielded needles of 5(?)-*bromo*-1-*methylbenzthiazole*, con-

taminated by a small quantity of gummy material which was removed by washing the crystals with ether, m.p. 120°. (Found: Br, 35·8. C_8H_6NBrS requires Br, 35·1 per cent).

Bromination of 5-bromo-1-aminobenzthiazole, the isolation of 3:5-dibromo-1-aminobenzthiazole hydrotribromide and the synthesis of 3:5-dibromo-1-aminobenzthiazole from 2:4-dibromophenylthiocarbimide by way of 2:4-dibromophenylthiocarbamide.—(A). Bromine (2 c.c. in 2 c.c. of chloroform) was added to a solution of 5-bromo-1-aminobenzthiazole (1 g.) in chloroform (60 c.c.) at 0°, and the mixture was kept in a freezing mixture when the *hydrotribromide* of 3:5-dibromo-1-aminobenzthiazole separated in beautiful golden plates which were collected on porous earthenware and dried in a vacuum. On heating the hydrotribromide lost bromine, becoming colourless, but was still unmelted at 285°. [Found: Br(total), 72·9; Br(labile), 30·3. $C_7H_4N_2Br_2S, HBr(Br_2)$ requires Br(total), 72·9; Br(labile), 29·2 per cent]. On reduction with sulphurous acid, basification with ammonia and recrystallisation from alcohol, 3:5-*dibromo-1-aminobenzthiazole* was obtained, m.p. 261°. (Found: Br, 51·9. $C_7H_4N_2Br_2S$ requires Br, 52·0 per cent).

(B). The 2:4-dibromoaniline used for the following experiments was conveniently prepared as follows:—A suspension of 20 g. finely powdered *p*-bromoacetanilide in cold potassium bicarbonate solution (10 g. in 400 c.c. of water) was mechanically stirred during the addition, drop by drop, of a hypobromous acid solution prepared from precipitated mercuric oxide (80 g.), bromine (20 c.c.) and water (600 c.c.). Stirring was continued for a further hour after completion of the addition of hypobromous acid and the mixture was extracted with chloroform. The *N*-bromo-*p*-bromoacetanilide, obtained by evaporation of the chloroform at laboratory temperature, was heated with a small quantity of glacial acetic acid in an oil-bath at 110-30°, and the cooled melt was recrystallised from alcohol. The dibromoacetanilide obtained in this way was hydrolysed with concentrated hydrochloric acid and the solution was basified with ammonia (*d* 0·880), when 2:4-dibromoaniline was obtained in small needles, m.p. 79°.

(i) 2:4-*Dibromophenylthiocarbimide*.—A solution of 2:4-dibromoaniline (5 g.) in chloroform (15 c.c.) was gradually added to a well-stirred suspension of thiocarbonyl chloride (5 c.c.) in water (80 c.c.). Stirring was continued for another ½ hour after the completion of addition of the amine and the mixture was extracted with chloroform.

On recrystallisation of the residue, obtained by removal of the chloroform on a steam bath, from benzene and thereafter from benzene-petroleum, the thiocarbimide was obtained in needles, m.p. 63°. (Found: Br, 54·5. $C_7H_3NBr_2S$ requires Br, 54·4 per cent).

(ii) 2:4-*Dibromophenylthiocarbamide*, prepared by heating a mixture of the dibromophenylthiocarbimide (2 g.), absolute alcohol (15 c.c.) and ammonia (*d* 0·880, 3 c.c.) for 20 minutes under reflux, separated from alcohol in prismatic needles, m.p. 171°. (Found: Br, 51·5. $C_7H_6N_2Br_2S$ requires Br, 51·6 per cent).

(iii) 1 G. of 2:4-dibromophenylthiocarbamide in chloroform (10 c.c.) was treated with bromine (1 c.c. in 1 c.c. of chloroform) and the mixture was heated on a steam bath under reflux for 15 minutes. As there was no separation of a hydroperbromide on cooling, the solution was concentrated in a vacuum and the product was reduced with sulphurous acid in the usual way. On crystallisation from alcohol, 3:5-dibromo-1-aminobenzthiazole was obtained as small needles, m.p. 259° which remained unaltered when mixed with the specimen obtained by bromination of 5-bromo-1-aminobenzthiazole.

3:5-*Dibromo*-1-*aminobenzthiazole tetrabromide*.—A saturated solution of 3:5-dibromo-1-aminobenzthiazole in 50 c. c. of chloroform was cooled and treated with bromine (3 c. c. in 3 c. c. of chloroform). As no separation of a bromo-addition compound occurred, the solution was concentrated in a vacuum at laboratory temperature, when the tetrabromide crystallised in glistening orange needles, which lost bromine on heating but were still unmelted at 285°. [Found: Br, (total), 76·95. $C_7H_4N_2Br_2S$ (Br_4) requires Br (total), 76·4 per cent]. A satisfactory determination of labile bromine could not be made owing to the very low solubility of the compound in chloroform. On reduction with sulphurous acid, the tetrabromide regenerated the original 3:5-dibromo-1-aminobenzthiazole.

Note on the action of bromine on thiobenzanilide.—In view of the formal similarity between Jacobson's synthesis of 1-substituted benzthiazoles from thioanilides and the preparation of 1-aminobenzthiazoles from arylthiocarbamides and bromine, it occurred to us that it might be possible to obtain 1-phenylbenzthiazole by treatment of thiobenzanilide in chloroform with bromine under the usual conditions of thiazole cyclisation of arylthiocarbamides. The following experiment was therefore made.— A solution of thiobenzanilide (0·5 g.) in chloroform (10 c. c.) was treated with bromine (0·5 c. c. in 0·5 c.c. of chloroform) and the mixture was heated on a water-bath under reflux for 10 minutes when hydrogen bromide was evolved, cooled

and concentrated under reduced pressure at laboratory temperature. The product obtained by reduction with sulphurous acid, basification with ammonia and recrystallisation from alcohol, however, differed strikingly from both 1-phenylbenzthiazole and 5-bromo-1-phenylbenzthiazole and melted at 206°. No trace of 1-phenylbenzthiazole, which is readily recognised when present in small quantities by its characteristic odour of tea roses, could be detected. It, therefore, appears that the duplicated thioamide triad system present in thiocarbamides, is necessary to thiazole cyclisation by bromine.

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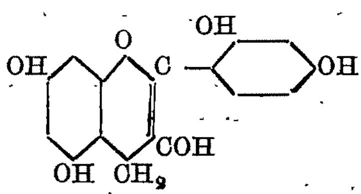
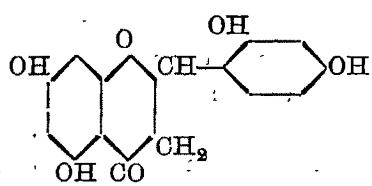
Studies in the Flavanone Series.

By Prafulla Chandra Mitter and Srish Kumar Saha.

In their investigation of the tinctorial properties of Jackwood, Perkin and Cope (*J. Chem. Soc.*, 1905, **87**, 715) found that Jackwood contains along with morin a second allied substance, called by them cyanomaclurin which is devoid of tinctorial property. When gently warmed with dilute alkali, it gives a beautiful indigo colouration. It has the formula $C_{15}H_{12}O_6$ and on fusion with alkali gives β-resorcylic acid and phloroglucinol. Perkin suggested that cyanomaclurin is possibly the reduction product of morin just as catechin is that of quercetin and assigned to it among others the following constitution:



But the above constitution has not been established definitely (*vide* Bhalla and Rây, *J. Chem. Soc.*, 1933, 288). It appeared to us worth while to consider the possibility of a flavanone structure for cyanomaclurin in view of the fact that flavanones have been found within recent times to occur largely among natural products.



It agrees well with the molecular formula and decomposition products. The characteristic colouration of flavanones with magnesium

powder and alcoholic hydrochloric acid, as was given by cyanomaclurin isolated in our laboratory, lent additional support to the above view. We, therefore, took up the synthesis of cyanomaclurin or at least the synthesis of a substance of the above constitution, which, even if it would fail to give synthetic cyanomaclurin itself, would settle after all one side of the question.

Our first attempt was to prepare the flavanone according to the method of Shinoda and others (*Chem. Zentr.*, 1928, II, 1885; 1930, I, 229) by condensing phloroglucinol in nitrobenzene solution in presence of aluminium chloride with 2:4-dihydroxycinnamoyl chloride with the OH groups suitably protected. 2:4-Dimethoxy-cinnamic acid was prepared at first but all attempts for its demethylation failed.

It has been found that resorcyl-β-aldehyde does not condense with malonic acid and attempts to prepare the dicarbomethoxy-cinnamic acid by condensing the dicarbomethoxy-β-resorcylaldehyde with malonic acid in pyridine solution in presence of piperidine also failed. Pyridine, in all probability, decarbomethoxylated the aldehyde and the hydroxy aldehyde thus produced could not condense with malonic acid.

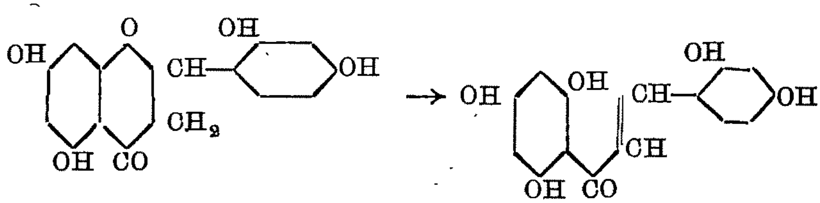
The condensation was next attempted in glacial acetic acid solution (Spath, *Monatsch*, 1920, 41, 271). Dicarbomethoxy-β-resorcylaldehyde was condensed with malonic acid in glacial acetic acid solution on a boiling water-bath for a varying number of hours 16, 8, 4, 2, 1). But in all cases the product instead of being 2:4-dicarbomethoxybenzalmalonic acid was found to be a mixture of two substances, 2:4-dicarbomethoxycinnamic acid (a trace) and carbomethoxyumbelliferone carboxylic acid. When boiled with sodium bicarbonate solution the latter gives umbelliferonecarboxylic acid, m.p. 262°, the carbomethoxy group being knocked off and the latter on heating gives umbelliferone, m.p. 225°.

Having no other alrernative it was decided to proceed with 2:4-dimethoxycinnamic acid which could be easily obtained in quantity. Attempts were also made to convert the above acid into the corresponding acid chloride but also to no purpose. PCl_3 was next added to the solution of the acid in benzene and allowed to react at a low temperature. On treatment with alcohol, the solution gave the ester of known melting point. All attempts to isolate the chloride, however, met with failure. It was too sensitive and decomposed on slight exposure to air. Further reaction was attempted

in situ. Nitrobenzene was added to the benzene solution of the acid chloride, benzene was distilled off under reduced pressure and to the nitrobenzene solution of the acid chloride phloroglucinol, dissolved in dry ether, was added in presence of $AlCl_3$. The condensation product, which was expected to contain the flavanone in question, was separated from nitrobenzene by steam distillation. It was dissolved in alkali and carbon dioxide was passed in. A very minute quantity of white slime was obtained which gave pink colouration with magnesium powder and alcoholic hydrochloric acid the well known test for flavanones. The flavanone, thus obtained, could not, however, by any means be collected in appreciable quantity and could not, therefore, be identified.

The acid chloride was next prepared in nitrobenzene solution directly and condensation was attempted but all in vain.

Attention was then directed to the synthesis of a product obtained by the fission of the ring of cyanomaclurin isolated from Jackwood in our laboratory and methylating the same.

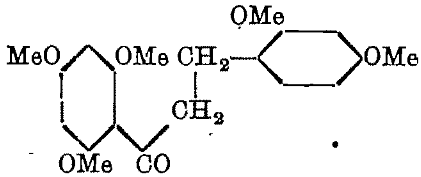


Cyanomaclurin (?). Chalkone (fission product).

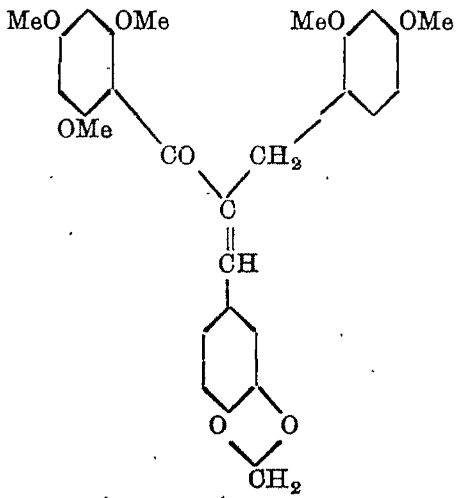
It was thought that if the assumption of cyanomaclurin having a flavanone structure be correct, the synthesis of the chalkone would produce valuable evidence in its support. Trimethylphloracetophenone, prepared from phloroglucinol trimethyl ether and acetyl chloride (Kostanecki and Tambor, *Ber.*, 1899, **32**, 2261) was condensed with dimethyl-β-resorcylaldehyde in presence of 10% NaOH giving 2:4:6:2′:4′-pentamethoxychalkone, m.p. 124°.

The chalkone, however, was not found identical with the substance isolated from Jackwood which had melting point near about 240°. It was supposed that the difference between the two might be due to geometrical isomerism as both the substances contain double bonds and that if the natural compound as well as the synthetic one be reduced, the two might become identical.

The synthetic chalkone, on reduction with hydrogen in presence of platinum oxide as catalyst, gave a saturated ketone, 2:4:6:2′:4′-pentamethoxydihydrochalkone.



The reduced ketone also combined with piperonal in presence of 10% caustic soda giving 2:4:6-trimethoxybenzoyl-2′:4′-dimethoxy-



benzyl-3″:4″-methylenedioxybenzylidenemethane.

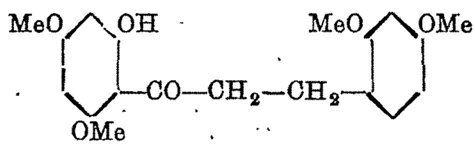
Attempts are now being made in this laboratory to collect the supposed natural pentamethoxychalkone in appreciable quantity which will be reduced and compared with the synthetic one.

The ease and readiness with which the chalkone was synthesised tempted us naturally to follow the classical method of Kostanecki's morin synthesis (*Ber.*, 1906, **39**, 625), so that having obtained some amount of 4:6:2′:4′-tetramethoxyflavanone by the method the expected cyanomaclurin would be obtained by one simple step of demethylation.

Dimethylphloracetophenone (*Ber.*, 1899, **32**, 2262) was condensed with dimethyl β-resorcylaldehyde giving 2-oxy-4:6:2′:4′-tetramethoxychalkone which melted sharply at 125° and not at 152° as recorded by Kostanecki.

Attempts were made to prepare the flavanone by ring closure according to Freudenberg's modification of Kostanecki's flavanone synthesis (*Ber.*, 1922, **55**, 1748). A small amount of crude flavanone was obtained melting between 160-68° (Kostanecki, 168°). But when attempt was made to recrystallise the substance, almost no flavanone was left behind.

The chalkone was reduced by means of hydrogen with platinum oxide as catalyst and gave 2-oxy-4:6:2′:4′-tetramethoxydihydrochalkone, m. p. 100°, which on methylation with methyl sulphate



and alkali gave a completely methylated ketone, m. p. 80°, which was found identical with the pentamethoxydihydrochalkone already prepared.

Experimental.

2:4-*Dimethoxycinnamic acid.*—2:4-Dimethoxy-β-resorcylaldehyde (8 g.) and malonic acid (12 g.) were dissolved in pyridine (24 c. c.) and a few drops of piperidine were then added and the mixture refluxed for an hour on a boiling water-bath, when CO_2 was evolved. The mixture was then heated for 5 minutes on a sand bath to complete the reaction, allowed to cool under the tap and acidified with hydrochloric acid (1:1), when there was copious white precipitate of the dimethoxycinnamic acid. It was collected, washed, dried and crystallised from acetic acid in white scales, m. p. 187°, yield 10 g. (Found: C, 63·38; H, 5·84; OCH_3, 30%; M. W. 210. $C_9H_6O_2(OCH_3)_2$ requires C, 63·46; H, 5·77; OCH_3, 29·8 per cent. M. W. 208.)

Dicarbomethoxy-β-resorcylaldehyde.—A solution of β-resorcylaldehyde (6·9 g.) in acetone (30 c.c.) was treated with methyl chlorocarbonate (4·7 g.) and under ice cooling and constant shaking *N*-NaOH (50 c. c.) were gradually introduced. 40 C. c. more of acetone were added and the solution treated with methyl chlorocarbonate and *N*-NaOH twice more with continuous cooling and constant shaking, when dicarbomethoxy compound began to separate. On addition of an equal quantity of water, the substance was obtained in quantitative yield and recrystallised from dilute acetone, m. p. 72°. (Found: C, 51·7; H, 3·8. $C_{11}H_{10}O_7$ requires C, 51·9; H, 3·9 per cent).

The *phenylhydrazone* crystallised from dilute alcohol in sandy crystals, m. p. 188°. (Found: N, 7·8. $C_{17}H_{16}O_6N_2$ requires N, 8·1 per cent).

The *semicarbazone*, prepared in the usual manner, crystallised from acetic acid in white sandy crystals, m. p. 185°. (Found: N, 13·2. $C_{12}H_{13}O_7N_3$ requires N, 13·5 per cent).

Dicarbomethoxy-β-resorcylic acid.—Potassium permanganate (2 g. in 83·2 c.c. of water) was added to a solution of dicarbomethoxy-β-resorcylaldehyde (2 g.) in acetone (16·6 c. c.) with constant shaking in the course of 30 to 45 minutes, the temperature being kept between 40-45° all throughout. The manganese dioxide was removed with SO_2 leaving a white precipitate of dicarbomethoxy-β-resorcylic acid, which was recrystallised from dilute acetone, m. p. 159°. (Found: C, 48·7; H, 3·7. $C_{11}H_{10}O_8$ requires C, 48·8; H, 3·7 per cent).

2:4-*Dicarbomethoxycinnamic acid and carbomethoxyumbelliferone carboxylic acid.*—Dicarbomethoxy-β-resorcylaldehyde (8 g.) and malonic acid (18 g.) were dissolved in glacial acetic acid (18 g.) and heated on a boiling water-bath (16 hours). On cooling the solution was diluted with water and the precipitate consisting of dicarbomethoxy-cinnamic acid and carbomethoxyumbelliferone carboxylic acid treated with 10% potassium bicarbonate solution under ice cooling. The cinnamic acid passed into solution, while the other remained insoluble. The filtrate was acidified with hydrochloric acid and recrystallised from dilute alcohol as beautiful white silky needles, m. p. 190°. (Found: C, 52·95; H, 3·82·$C_{13}H_{12}O_8$ requires C, 52·7; H, 4·07 per cent). The residue was crystallised from acetic acid as beautiful white needles, m. p. 201-02°. (Found: C, 54·84; H, 3·11. $C_{12}H_8O_7$ requires C, 54·54; H, 3·03 per cent).

Carbomethoxyumbelliferone carboxylic acid (2 g.) was boiled with an excess of 10% sodium carbonate solution for 15 minutes. A highly blue fluorescent solution was obtained which on acidification with hydrochloric acid (1:1) gave a white precipitate of umbelliferone carboxylic acid, which crystallised from alcohol, m.p. 262° and when heated 4—5° above its m. p. for 15 minutes gave umbelliferone, m.p. 225°. (Found: C, 63·0; H, 2·9. Calc: C, 58·2; H, 2·9 per cent).

2: 4: 6: 2′: 4′-*Pentamethoxychalkone.*—Caustic soda (5%, 10 g.) solution was added to a solution of phloracetophenone trimethyl ether (5 g.) and dimethyl-β-resorcylaldehyde (4 g.) in alcohol (50 c.c.). After standing for a time in a warm place, the whole solidified to a yellow mass. This was poured into dilute hydrochloric acid and the

precipitate was collected and pressed on a porous plate and crystallised from alcohol in pale yellow crystals, m.p. 124°, yield 5 g (Found: C, 66·8; H, 6·0. $C_{20}H_{22}O_6$ requires C, 67·04; H, 6·14 per cent).

2 : 4 : 6 : 2′ : 4′-*Pentamethoxydihydrochalkone*.— A solution of the pentamethoxychalkone (5 g.) in pure ethyl acetate (100 c.c.) was taken in a hydrogenation flask with platinum oxide (0·1 g.) added as catalyst. The flask was evacuated and connected with the hydrogen cylinder and shaken, when absorption of hydrogen took place. In about 3 hours theoretical amount of hydrogen was absorbed when the flask was disconnected and the solution filtered from the platinum oxide through a Gooch. Ethyl acetate was distilled off on the water-bath and a thick oil was obtained which solidified to a mass of colourless crystals after a time. It crystallised from dilute alcohol in well-defined colourless rhombic plates, m.p. 80°, yield theoretical. (Found: C, 66·06; H, 5·9. $C_{20}H_{24}O_6$ requires C, 66·6; H, 6·6 per cent).

The *oxime*, prepared in the usual manner, crystallised from dilute alcohol as shining colourless crystals, m. p. 142°. (Found: N, 3·4. $C_{20}H_{25}O_6N$ requires N, 3·7 per cent).

The *semicarbazone* crystallised from alcohol, m.p. 184°. (Found: N, 13·0. $C_{21}H_{27}O_6N_3$ requires N, 13·1 per cent).

2 : 4 : 6-*Trimethoxybenzoyl-2′ : 4′-dimethoxybenzyl-3″ : 4″-methylenedioxybenzylidenemethane*. —2 : 4 : 6-Trimethoxybenzoyl-2 : 4-dimethoxybenzylmethane (1 g.) and piperonal (0·4 g.) were dissolved in alcohol (10 c.c.) and to the warm solution NaOH solution (50%, 2 g.) was added. After standing for a time in a warm place, the whole solidified to a pale yellow mass. This was then poured into dilute hydrochloric acid and filtered. The product crystallised from acetic acid in shining crystals, m. p. 215°, yield 1 g. (Found: C, 68·0; H, 5·4. $C_{28}H_{28}O_8$ requires C, 68·29; H, 5·69 per cent).

2-*Oxy-4 : 6 : 2′ : 4′-tetramethoxychalkone*.—To the warm solution of phloracetophenone dimethyl ether (2 g.) and dimethyl-β resorcylaldehyde (1·6 g.) in alcohol (20 c.c.) NaOH solution (50%, 4 g.) was added. After standing for a short time the whole solidified to an intense yellow mass. This was then just neutralised with dilute hydrochloric acid and the precipitate collected, pressed on a porous plate and crystallised from alcohol in yellow crystals, m.p. 125°, the melting point does not change in the least even after repeated crystallisations for six times (Kostanecki, m. p. 152°). (Found: C,

66·43; H, 5·84; OMe, 36·0. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·80; OMe, 36·5 per cent).

2-Oxy-4 : 6 : 2′ : 4′-Tetramethoxydihydrochalkone. — The hydroxytetramethoxychalkone (2 g.) was dissolved in pure ethyl acetate (80 c.c.) and was then reduced by means of hydrogen with platinum oxide (0·05 g.) as catalyst exactly in the same manner as in the reduction of 2 : 4 : 6 : 2′ : 4′-pentamethoxychalkone. On distilling off the ethyl acetate a thick oil was obtained which readily solilidified on rubbing with a little ether to canary yellow crystals. It crystallised from ether, m. p. 100°. On methylation with methyl sulphate and alkali it gave 2 : 4 : 6 : 2′ : 4′-pentamethoxydihydrochalkone which proves to be identical with the pentamethoxy saturated ketone synthesised before. (Found : C, 65·5; H, 5·90. $C_{19}H_{22}O_6$ requires C, 65·8; H, 6·30 per cent).

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On the Oxidising Enzymes in Betel Leaves (*Piper Betel*).

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Oxidation and oxidising enzymes play a very important rôle in the plant and animal kingdom and it is not surprising, therefore, that a large amount of experimental work and theoretical discussion have centeed round the process of biological oxidation. In the 19th century we come across the theories of M. Traube, Engler, Palldin and Bach on oxidation. At present a great controversy is going on between Warburg ("Katalytische Wirkungen der lebendigen Substanz", Berlin, 1928) and Wieland (Oppenheimer, "Handbuch der Biochemie", 1925, Vol. 2, pp. 252-72) about the mechanism of biological oxidation. Warburg maintains that biological oxidation is due in all cases to an activation of oxygen brought about by the respiratory ferment which contains iron and which is like hämin in its constitution. Hydrocyanic acid inhibits biological oxidation because according to Warburg it combines with and inactivates the iron of the respiratory ferment.

Wieland on the other hand holds that the action of the oxidising enzymes, dehydrogenase as he calls them, consists in activating the hydrogen of the oxidisable substance (called donator) and this hydrogen of the donator combines with a suitable substance present in most cases and this latter substance is oxygen (called the acceptor). The primary product formed is hydrogen peroxide which is at once decomposed by the ferment catalase which is present in all cells. The inhibiting action of hydrocyanic acid is according to Wieland due to its retarding effect on catalase. That oxygen can be replaced by other suitable acceptors has been shown by Thumberg (*Arch. Physiol.*, 1921, **182**, 601; *Scand. Arch. Pysiol.*, 1928, **54**, 6) who has experimentally demonstrated that in biological oxidations methylene blue can very well replace oxygen.

Recently Keilin (*Proc. Roy. Soc.*, 1929, **B**, **104**, 206, 250) by his work on the cytochrome of the cell has tried to co-ordinate the theories of Wieland and Warburg; according to Keilin the main

respiratory system of the cell comprises the following components: (*a*) dehydrogenase, (*b*) metabolites, (*c*) cytochrome, (*d*) molecular oxygen.

It is clear that investigation of oxidising systems in varied and simple systems will ultimately enable us to gain an insight into the nature of oxidising enzymes and the mechanism of oxidation.

An investigation of the oxidising enzymes in betel leaves which are so common in India was therefore taken up.

EXPERIMENTAL.

Betel leaves were washed thoroughly under tap water and finally with distilled water so as to free from adhering foreign matters. Then they were cut into small pieces and rubbed in an iron mortar. The juice was then pressed out of the mass by means of a pressing machine. It was then kept in a clean sterile vessel and was centrifuged for about 30 minutes. The juice was then ready for experiments. It was found to be acidic and was neutralised exactly with caustic soda solution ($N/2$). It was then brought to desired p_H value by adding necessary amounts of acid or alkali using Clark and Lubb's series of indicators. 5 C.c. of juice of any suitable p_H of the solution was kept at constant p_H with $M/10$-phosphate buffer. Thus the reaction mixture contained 10 c.c. substrate solution, 5 c.c. betel leaf juice, 2 c.c. buffer and 1 c.c. water in a Barcroft-Warburg respirometer. The same sample of betel juice was used for experiments with the same substrate which was carried out simultaneously.

Apparatus.—The apparatus that was set up for oxidation measurements was a series of 8 Barcroft-Warburg respirometers which could be moved in a thermostat. The fall of pressures with the absorption of oxygen was indicated by the manometers, which were filled up with Brodie's solution.

Each vessel was provided with a reservoir containing caustic potash solution to absorb carbon dioxide.

A knowledge of the volume of the vessels is necessary to find out the volume of oxygen absorbed from the noted difference. The constant K of the vessel is calculated according to the following formula of Warburg.

$$K = \frac{\frac{273}{T} V_G + V_F \, a}{P_0}$$

Where V_a is the volume of the vessel, V_F that of the liquid in the vessel, T the absolute temperature, P_o, the normal pressure (10,000 mm. Brodie) and a, the absorption coefficient of the gas that disappears. The volume V of oxygen that is used up in oxidation is given by $Kh = V$, where h is the difference of pressure registered by the manometer.

One Barcroft vessel contained only water of the same volume as in other vessels to correct for the changes in temperature. Another vessel contained only betel juice at the desired p_H with buffer to find out the amount of oxygen, if any, absorbed by the juice itself. In both cases the correction necessary was found to be very small and always taken into account.

Action of the betel juice on different substrates *e.g.* hydroquinone, leucine, succinic acid, acetaldehyde, linoleic acid and oleic acid was tried. The temperatures employed were 34·4° and 25°. A stock solution of each substance was prepared and 10 c.c. of this substrate solution brought to the desired p_H before each experiment. As already indicated the total volume of reaction mixture was 18 c.c.

It must be made clear at the outset that the oxidising capacity of different samples of juice was different, the limits of variation being about 50%. The experiments with each substrate, however, were carried out with one and the same sample, and at the same time. The following tables indicate the results.

The following abbreviations have been used in the tables: t= time in min., P_d=pressure difference in cm., K=vessel constant and V_o =volume of oxygen absorbed in c.c.

TABLE I *a*.

Hydroquinone.

Temp. =25°. Strength of stock solution=2%.

	p_H 4·49 K=0·0057		p_H 5·2 K=0·0051		p_H 6·2 K=0·0049		p_H 6·8 K=0 0061	
t	P_d.	V_o.	P_d.	V_o.	P_d.	V_o.	P_d.	V_o.
10	4·4	0·02508	5·8	0·02958	5·6	0·02744	4·5	0·02745
35	18·6	0·10402	22·4	0·11424	20·8	0·10192	15·1	0·09211
60	35·3	0·20121	37·6	0·19176	35·4	0·17346	25·1	0·15817

TABLE I *b*.

Temp. = 34·4°.

t.	p_H 4·49 K = 0·0055 $P_{d.}$	$V_{o.}$	p_H 5·2 K = 0·005 $P_{d.}$	$V_{o.}$	p_H 6·2 K = 0·0048 $P_{d.}$	$V_{o.}$
10	5·5	0·03025	6·4	0·0320	5·4	0·02592
35	16·7	0·09185	19·1	0·0955	16·0	0·0768
60	27·9	0·15345	31·6	0·1580	27·2	0·13056

It will be evident from the above experiments that p_H optimum for the enzyme action in the case of hydroquinone is in the neighbourhood of p_H 5. It should be mentioned here that hydroquinone alone suffers very little oxidation when shaken in a Barcroft vessel.

Temperature has very little effect on the enzymatic oxidation of hydroquinone, as is evident from the above tables.

TABLE II *a*.

Leucine.

Temp. = 25°. Strength of stock solution = 0·2%.

t.	p_H 4·494 K = 0·0057 $P_{d.}$	$V_{o.}$	p_H 5·239 K = 0·0051 $P_{d.}$	$V_{o.}$	p_H 6·2 K = 0·0049 $P_{d.}$	$V_{o.}$
10	2·9	0·01653	4·5	0·02295	3·2	0·01568
35	5·5	0·03135	7·8	0·03978	6·0	0·0294
60	6·5	0·03605	9·0	0·0459	7·0	0·0343
90	8·5	0·04845	10·1	0·05151	9·0	0·0441

TABLE IIb.

Temp. = 34·4°.

	p_H 4·49, K = 0·0055		p_H 5·2, K = 0·005		p_H 6·2, K = 0·0048		p_H 6·8, K = 0·0055	
t.	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$
10	3·4	0·0187	3·8	0·0190	4·8	0·02304	3·2	0·01760
35	5·6	0·0308	6·2	0·0312	5·9	0·02832	4·9	0·02695
73	7·6	0·0418	8·4	0·0420	8·2	0·03986	7·5	0·04126
120	9·0	0·0495	10	0·0500	10·3	0·04944	9·0	0·64950

In this case also the optimum p_H equals to 5·2.

TABLE IIIa.

Succinic acid.

Temp. = 25°. Stock solution = 1% soln.

	p_H 4·49, K = 0·0057		p_H 5·2, K = 0·0051		p_H 6·2, K = 0·0049	
t.	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$
10	1·7	0·00969	3·3	0·01683	2·7	0·01323
35	3·7	0·02109	5·8	0·02958	6·0	0·0294
60	4·9	0·02793	8·4	0·04284	7·0	0·0348
120	6·6	0·03762	10·0	0·05100	8·3	0·04067

TABLE IIIb.

Temp. = 34°.

	p_H 4·49, K = 0·0055		p_H 5·2, K = 0·005		p_H 6·2, K = 0·0048		p_H 6·8, K = 0·0055	
t.	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$
10	3·3	0·01815	4·9	0·0245	5·3	0·02544	2·7	0·01485
35	6·5	0·03575	8·7	0·0435	8·2	0·03936	5·8	0·03190
60	8·0	0·0440	10·1	0·0505	10·0	0·0480	7·8	0·0429

p_H 5·2 is again the optimum point.

TABLE IV *a*.

Acetaldehyde.

Temp. = 25°. Strength of stock solution = $M/2$.

	p_H 4·49 $K = 0·00557$		p_H 5·2 $K = 0·0057$		p_H 6·2 $K = 0·0057$	
t.	*Pd*.	V_0.	*Pd*.	V_0.	*Pd*.	V_0.
10	6·1	0·03477	7·0	0·0357	7·2	0·04104
35	7·5	0·04275	9·0	0·0459	10·0	0·057
60	8·0	0·0456	9·4	0·04794	10·2	0·05814
120	9·8	0·05586	11·0	0·0561	11·6	0·06612

TABLE IV *b*.

Temp. = 34·4°.

	p_H 4·49 $K = 0·0055$		p_H 5·2 $K = 0·0048$		p_H 6·2 $K = 0·0055$	
t.	*Pd*.	V_0.	*Pd*.	V_0.	*Pd*.	A_0.
10	9·0	0·0495	10	0·048	9·7	0·05335
35	10·2	0·0561	12	0·0576	11·1	0·06105
60	10·9	0·05995	12·6	0·06048	11·9	0·06545
90	11·4	0·06270	12·8	0·06124	12·6	0·06930

The optimum p_H is 6·2 and there is an appreciable temperature coefficient.

Linoleic and oleic acids.—It was found that these two acids dissolved in a solution of sodium taurocholate and sodium chloride. Presence of lecithin slightly increased the solubility of these two acids. Blank experiments showed that neither taurocholate nor lecithin was oxidised either alone or in presence of betel juice. Experiments were done with and without lecithin. Lecithin had a slight accelerating effect on the oxidation of linoleic acid in presence of betel juice but a retarding effect on the oxidation of oleic acid.

TABLE V *a*.

Linoleic acid.

Temp. = 25°. Stock solution = 1 c.c. linoleic acid in 100 c.c. soln. containing 5g. Na-taurocholate and 1g. NaCl.

	p_H 4·49 K=0·0057		p_H 5·2 K=0·0051		p_H 6·2 K=0·0049	
t.	*Pd*.	*Vo*.	*Pd*.	*Vo*.	*Pd*.	*Vo*.
10	3·7	0·02109	5·0	0·0255	4·0	0·0196
35	5·9	0·03363	7·4	0·03774	6·2	0·03033
60	7·3	0·04161	9·6	0·04896	8·0	0·0392
90	9·0	0·0513	11·2	0·05712	10	0·0490

TABLE V*b*.

Temp. = 34·4°.

	p_H 4·49 K=0·0055		p_H 5·2 K=0·005		p_H 6·2 K=0·0048		p_H 6·8 K=0·0055	
t.	*Pd*.	*Vo*.	*Pd*.	*Vo*.	*Pd*.	*Vo*.	*Pd*.	*Vo*.
10	2·4	0·01326	3·0	0·015	3·3	0·01584	1·4	0·0077
35	4·5	0·02475	5·5	0·0275	5·9	0·02832	3·6	0·01910
60	5·6	0·03089	7·0	0·0350	7·4	0·03552	4·5	0·02475
120	7·6	0·04180	9·5	0·0475	10·0	0·0480	6·0	0·0330

TABLE VI.

Linoleic acid with lecithin.

Stock solution same as in Table V*a* but contains a trace of lecithin.

Temp. = 34·4°.

	p_H 4·49 K=0·0055		p_H 5·2 K=0·0048		p_H 6·2 K=0·0055	
t.	*Pd*.	*Vo*.	*Pd*.	*Vo*.	*Pd*	*Vo*.
13	3·0	0·0165	4·2	0·02016	4·1	0·02255
35	6·5	0·03575	7·1	0·03408	7·0	0·0385
60	8·9	0·04895	9·0	0·0432	8·6	0·04730
90	10·2	0·05610	10·1	0·04848	9·7	0·05335

TABLE VII *a*.

Oleic acid.

Stock solution 1 c.c. dissolved in 100 c.c. solution of 5 g. Na-taurocholate and 0·9 g. NaCl. Temp. = 25°.

	p_H 4·49 $K = 0·0057$		p_H 5·2 $K = 0·0051$		p_H 6·2 $K = 0·0049$	
t.	P_d.	V_o.	P_d.	V_o.	P_d.	V_o.
10	4·0	0·0228	4·6	0·02844	4·5	0·02205
35	5·7	0·03249	6·4	0·03263	6·3	0·03087
60	6·0	0·0342	6·8	0·03468	6·7	0·03283
120	7·2	0·04104	8·6	0·04437	8·0	0·0384

TABLE VIIb.

Temp. = 34·4°.

	p_H 4·49 $K = 0·0055$		p_H 5·2 $K = 0·005$		p_H 6·2 $K = 0·0048$	
t.	P_d.	V_o.	P_d.	V_o.	P_d.	V_o.
10	5·4	0·02970	5·7	0·0285	5·3	0·02544
35	9·6	0·05180	10·7	0·0535	10·0	0·04800
60	11·0	0·06050	12·7	0·0635	12·4	0·05952

TABLE VIII.

Oleic acid with lecithin.

Stock solution same as in Table VII*a* but contains a trace of lecithin. Temp. = 34·4°.

	p_H 4·49 $K = 0·0055$		p_H 5·2 $K = 0·005$		p_H 6·2 $K = 0·0046$	
t.	P_d.	V_o.	P_d.	V_o.	P_d.	V_{O_2}
10	1·3	0·00715	1·5	0·0075	1·2	0·00576
35	3·8	0·01930	4·2	0·0210	3·9	0·01872
60	5·5	0·03025	6·2	0·0310	5·9	0·02832
120	8·0	0·0440	8·9	0·0445	9·3	0·04467

Effect of potassium cyanide on the oxidation.—Effect of potassium cyanide, brought upto the desired p_H on the

oxidation of hydroquinone and acetaldehyde in presence of betel juice was also tried. In both cases a retardation was obtained but the reaction did not completely stop. In the case of hydroquinone a 75% retardation was obtained. In the case of acetaldehyde oxidation as the hydrocyanic acid concentration varied from $M/360$ to $M/1440$ the retardation varied from 45% to 20%. Thus the retardation by hydrocyanic acid is of a much lower order than that expected on Warburg's hypothesis.

In the case of acetaldehyde the effect of changing its concentration keeping that of hydrocyanic acid constant was also tried. It was found that with the increased concentration of acetaldehyde the retardation by hydrocyanic acid decreased. This can be explained by assuming that the aldehyde cyanhydrin has got no retarding effect and as the concentration of the acetaldehyde increases that of the cyanhydrin also increases. Similar results were obtained by Wieland and Bertho in their experiments on the effect of hydrocyanic acid on acetic acid fermentation (*Annalen*, 1928, **467**, 95). The following tables indicate the results:

TABLE IX.

Effect of KCN *on hydroquinone.*

Temp. = 34°. Each vessel contains 10 c.c. of 2% hydroquinone, 5 c.c. betel leaf juice, 2 c.c. buffer, 1 c.c. $M/500$-KCN or water.

Time.	KCN.	Pressure diff.	p_H.	K.	O_2 absorbed.
10 min.	absent	16·3 cm.	4·49	0·005	0·0815 c.c.
20		31·0			0·1550
60		31·5			0·1575
10	present	3·9	4·49	0·0048	0·001872
20		7·6			0·03648
60		9·3			0·04462
10	absent	12	6·2	0·0061	0·0732
20		21·4			0·13054
60		24·5			0·14945
10	present	4·2	6·2	0·0051	0·02142
20		7·9			0·04029
60		9·1			0·04641

TABLE X.

Effect of KCN *on acetaldehyde.*

Concentration of acetaldehyde was kept constant while that of KCN was changed. Each vessel contained 10 c c. of $M/2$-acetaldehyde, 5 c.c. betel juice, 2 c.c. buffer, and 1 c.c. KCN soln. Temp. = 34°. p_H 6·2.

	$K=0·005$ $M/360$-KCN		$K=0·0448$ $M/720$-KCN		$K=0·006$ $M/1440$-KCN		$K=0·0051$ KCN-nil.	
t.	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{o.}$	$V_{o.}$
10	6·9	0·0345	7·5	0·036	8·6	0·0516	13·5	0·06885
35	9·5	0·0475	10·1	0·04848	10·7	0·0642	15·7	0·08007
60	10·1	0·0505	11·0	0·05280	11·2	0·0666	16·6	0·08466
120	11·1	0·0555	13·0	0·0624	11·5	0·0690	17·0	0·0867

TABLE XI.

Effect of KCN *on acetaldehyde.*

Concentration of acetaldehyde was varied while that of KCN kept constant. Each vessel contained 10. c.c. of acetaldehyde of requistite strength, 5 c.c. betel juice, 2 c.c. buffer, 1 c.c. $M/20$-KCN. Temp. = 34°. p_H 6·2.

	$K=0·005$ $M/72$-aldehyde		$K=0·0048$ $M/36$-aldehyde		$K=0·006$ $M/18$-aldehyde		$K=0·0051$ $M/18$-aldehyde	
t.	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$	$V_{o.}$	$P_{d.}$ *without* KCN.	$V_{o.}$
10	4·4	0·022	5·1	0·02448	5·5	0·033	10·0	0·051
20	5·0	0·025	6·0	0·0288	6·1	0·0366	10·6	0·05406
40	6·1	0·0305	7·3	0·03504	7·3	0·0438	12·1	0·06171
60	6·7	0·0335	8·0	0·0384	7·5	0·045	12·4	0·06324
120	8·9	0·0445	9·8	0·04704	8·1	0·0522	14·4	0·07344

On the catalase present in betel juice.—Some experiments were carried out to determine the catalase present in the betel juice. For this purpose the juice prepared, clarified and brought to the desired p_H as in the previous experiments, was employed. An acetate buffer

of p_H 5·8 was used. Each Barcroft vessel contained 10 c.c. of $M/40$ hydrogen peroxide solution at p_H 5·8, 5 c.c. of betel juice at p^H 5·8, 2 c.c. of acetate buffer and 1 c.c. of water brought to p_H 5·8. The catalase decomposed H_2O_2 liberating oxygen and that caused an increase in pressure which was noted. Table XII shows the results.

TABLE XII.

Temp. =34·4°.

Time.	Pressure diff.	p_H.	K.	O_2 liberated.
10 mins.	17 cm.	5·8	0·0051	0 0867 c.c.
35	28			0·1428
60	37			0·1887
80	46			0 2346

Effect of hydrocyanic acid on betel juice catalase was also tried. Along with the above mentioned experiment three other experiments were simultaneously carried out in which 1 c.c. of water was replaced by 1 c.c. of KCN of different strength, but all brought up to p_H 5·8. The results in Table XIII show considerable retardation of catalase action.

TABLE XIII.

Effect of hydrocyanic acid on catalase.

Each vessel contains 10. c.c. of $M/40$-H_2O_2, 5 c.c. of betel leaf juice, 2 c.c. of acetate buffer, 1 c.c. of KCN. Temp. =34·4°.

Time.	Conc. of KCN.	Pressure diff.	p_H.	K.	O_2 liberated.
10 min.	$M/360$	5·5 cm.	5·8	0·005	0·02725 c.c.
35		5·5			0·055
60		14·6			0·073
120		20·8			0·104
10	$M/720$	6·3	5·8	0·0048	0·03024
35		12·1			0·05808
60		16·0			0·0768
120		21·2			0·10176
10	$M/1440$	7·2	5·8	0·0059	0·04248
35		14·3			0·08437
60		14·8			0·10502
120		22·0			0·1298

Discussion.

It is clear from the above experiments that betel juice is capable of bringing about the oxidation of many substances. It is scarcely possible that a single enzyme is active in all cases ; a difference in p_H optimum also points to that.

As regards the mechanism of oxidation Warburg's theory alone is scarcely sufficient to explain all the observations. Hydrocyanic acid does not completely inhibit the oxidation. On the other hand the inhibition of oxidation by hydrocyanic acid appears to be of the same order as the inhibitions of catalase action by hydrocyanic acid. This lends strong support to the views of Wieland according to whom hydrogen peroxide is the primary product of all biological oxidations in oxygen which is at once decomposed by the catalase present.

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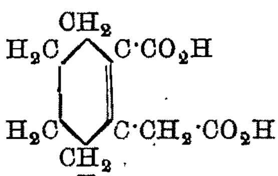
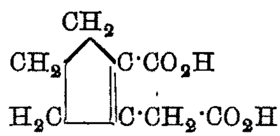
Synthesis of Δ^2-*cyclo*Pentene-1 : 3-dicarboxylic Acid : Its Relation to Glutaconic Acid Derivatives.

By Birendra Lal Nandi.

It has been shown by Kon and Nanji (*J. Chem. Soc.*, 1932, 2426) that the ability to exist in stereoisomeric forms is not essential to glutaconic character. Thus the cyclic glutaconic acid derivatives (I) and (II), in which stereoisomerism is precluded due to ring formation, behave like ordinary $\alpha\beta$-disubstituted glutaconic acids. They form hydroxy anhydrides and their esters yield stable potassio derivatives and can be readily methylated.


(I)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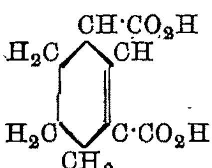
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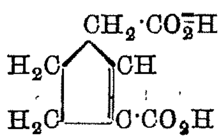
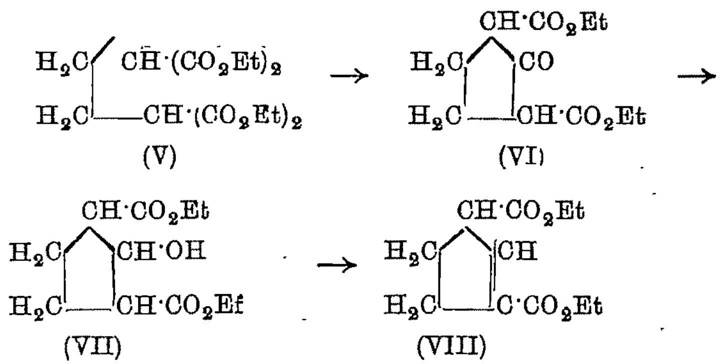

(IV)

Further support has been put forward by a recent paper (Kon and Nandi. *J. Chem. Soc.*, 1933, 1628) by synthesising and studying the properties of the Δ^3-tetrahydro*iso*phthalic acid (III) and its ester. Though the acid (III) does neither form a neutral nor an enolic anhydride, its ester can readily be alkylated proving the presence of a mobile hydrogen atom

The present investigation was undertaken to synthesise the Δ^2-*cyclo*pentene-1 : 3-dicarboxylic acid (IV) in order to compare its character with that of glutaconic acid derivatives. It may be mentioned here that this acid (IV) is a true $\alpha\gamma$-disubstituted glutaconic acid in which the two carbon atoms of the propene chain are

part of the five-membered ring. The synthesis has been effected by the following method.

Ethyl butane tetracarboxylate (Perkin, *J. Chem. Soc.*, 1894, **65** 578) was cyclised in presence of sodium ethoxide, following the method of Uschakov (*J. Russ. Phys. Chem Soc.*, 1929, **61**, 795), and then decomposed with dilute acid giving rise to (VI) with elimination of ethyl carbonate. The ketonic ester was then reduced by means of



hydrogen in presence of platinum oxide and the hydroxy ester dehydrated to ethyl $\triangle^2$-*cyclo*pentene-1 :3-dicarboxylate (VIII). Cold alkaline hydrolysis of this ester gave the unsaturated acid (IV).

A second attempt to synthesise ethyl $\triangle^2$ -*cyclo*pentene-1 :3-dicarboxylate by the condensation of ethyl $\triangle^1$-*cyclo*pentene carboxylate with ethyl oxalate, an observation of Lapworh (*J. Chem. Soc.*, 1901, **79**, 1265) who studied the condensation of ethyl oxalate with ethyl crotonate and similar esters containing the system $—CH_2-\overset{|}{C}=\overset{|}{C}-CO-$, was unsuccessful under various experimental conditions (*vide* Kon and Nandi, *loc. cit.*).

Ethyl $\triangle^2$-*cyclo*pentene-1 :3-dicarboxylate formed a stable sodio derivative and could be readily methylated. The methylated ester was hydrolysed to the corresponding acid (IV). The acid appeared to be quite stable to alkali like $\triangle^2$-tetrahydro*iso*phthalic acid and the acid was recovered unchanged after 7 days' boiling with 20% potassium hydroxide solution. Attempts were made to prepare a neutral or an enolic anhydride without success. This result is not surprising as it can be shown from a model that an acid of this type should not give an anhydride readily.

Thus all the cyclic glutaconic acids (I, II, III & IV), in which stereoisomerism is precluded due to ring formation, display the

properties characteristic to the glutaconic acid derivatives. With the observed facts it can be deduced that, in glutaconic acid derivatives tautomerism and stereoisomerism are independent of each other. Though the isomerides could not be isolated in acids (I) and (II) (the terminal carbon atoms in acids III and IV being symmetrical, the isomerides are identical) still they showed the presence of a mobile hydrogen atom which was responsible for the so-called 'glutaconic character.'

EXPERIMENTAL.

Ethyl cyclo*pentanone*-2:5-*dicarboxylate* (VI).—A mixture of ethyl malonate (960 g.) and ethylene dichloride (315 g.) was slowly added to a cold solution of sodium (138 g.) in absolute alcohol (1932 c. c.) and the whole was thoroughly mixed by shaking for 10 minutes as a jelly like mass might be formed. The mixture was transferred into pressure bottles (8), securely corked and tied down and heated on a steam-bath for 12 hours. The alcohol was removed under reduced pressure and the residue was taken up in ether. The ethereal solution was washed thoroughly with dilute sodium carbonate solution, acid and then water. After removal of ether the brown residual oil was distilled in portions of about 100 c.c. The fraction b. p. 150-192°/8 mm. was redistilled giving 250 g. of pure ethyl butane tetracarboxylate, b.p. 170-190°/5 mm.

The above ester (180 g.) was added to sodium (13 g.) in 260 c.c. of alcohol (dried over calcium) and boiled under reflux for 8 hours. The alcohol and ethyl carbonate were removed under reduced pressure, 200 c.c. of water added and the solution cooled in a freezing mixture and slowly decomposed (below 5°) by addition of 60 c.c. of 20% sulphuric acid. The oil was extracted with ether, washed with sodium carbonate solution and then with water and the ether removed. On distillation some unchanged initial material was obtained together with a lower fraction, b.p. 150-185°/26 mm. which on refractionation gave 80 g. of the ester (VI), b.p. 169-175°/18 mm. It gave intense red colouration with ferric chloride. d_4^{30}, 1·811 ; n_D, 1·4567 ; $[R_L]_D$, 54·86; (calc. 54·55). (Found: C, 57·8 ; H, 7·0. $C_{11}H_{16}O_5$ requires C, 57·9; H, 7·0 per cent).

Ethyl cyclopentanol-2:5-dicarboxylate (VII).—30 G. of the ketonic ester were mixed with 200 c.c. of rectified spirit, 1 c.c. of ferrous chloride solution (0·18 g. per litre) and 2 g. of platinum oxide catalyst)-"Organic Synthesis," vol. 8, p. 92) were added to it and shaken with hydrogen. The theoretical volume of hydrogen was absorbed in 8 hours. The catalyst was filtered off, the solvent removed under reduced pressure and the residue distilled at 173-175°/27mm, yield 25 g.

Ethyl $\triangle^2$-cyclo*pentene*-1:3-*dicarboxylate* (VIII).—25 G. of the hydroxy ester (VII) in 20 g. of pyridine were cooled in a freezing mixture and 14 g of thionyl chloride introduced drop by drop with constant shaking. After 12 hours, water was added and the ester extracted with ether. The unsaturated ester had b.p. 168°/21 mm, yield 18 g. $d_4^{24\cdot8}$, 1·1121; n_D, 1·4564; $[R_L]_D$ 54·84; (calc. 53·97). (Found: C, 62·1 ; H, 7·4. $C_{11}H_{16}O_4$ requires C, 62·2 ; H, 7·5 per cent).

Ethyl $\triangle^1$-*cyclo*pentene carboxylate was prepared from *cyclo*pentanone essentially as described by Kon and Nandi (*loc. cit.*) in the preparation of ethyl tetrahydrobenzoate. The dehydration of the cyanhydrin was best effected by means of P_2O_5 in benzene (55%). The use of thionyl chloride alone as dehydrating agent (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 399) was found unsuccessful, while pyridine and thionyl chloride gave an yield of 10% of the unsaturated cyanide, b. p. 68°/22 mm. 42 G. of the unsaturated cyanide were refluxed for 12 hours with 170 c.c. of absolute alcohol and 70 c.c. of concentrated sulphuric acid. The unsaturated ester distilled at 71°/11 mm., yield 30 g.

All attempts to condense ethyl oxalate with ethyl $\triangle^1$-*cyclo*pentene carboxylate failed when sodium or potassium was used in neutral medium (benzene or toluene) or in alcohol (Kon and Nandi, *loc. cit.*).

$\triangle^2$-cyclo*Pentene*-1:3-*dicarboxylic acid* (IV).—10 G. of the ester (VIII) were left at room temperature with 4·5 g. of caustic soda in 20 c.c. of water and 25 c.c. of alcohol. After 2 days the alcohol was removed under reduced pressure, the solution diluted, acidified with dilute sulphuric acid, evaporated to dryness and extracted with acetone. The acid, m.p. 150·5°, insoluble in ether, was crystallised from hot water in irregular plates. (Found: C, 55·8; H, 5·0. $C_7H_8O_4$ requires C, 53·8; H, 5·1 per cent).

Methylation.—10 G. of the pure unsaturated ester (VIII) were left overnight with 1·1 g. of molecular sodium in 10 c.c. of dry benzene; as only a part of the metal had dissolved, the mixture was boiled on the steam bath for 6 hours. An excess of methyl iodide was then added and the vigorous reaction completed by heating for an hour. The isolated ester could not be distilled without decomposition. It was hydrolysed with caustic potash solution by boiling for an hour. The methylated acid was extracted with ether in a continuous extractor and crystallised from water (charcoal) in fine white crystals, m.p. 225° (decomp.). (Found: C, 56·4; H, 5·7. $C_8H_{10}O_4$ requires C, 56·4; H, 5·8 per cent).

Action of alkali on acid (IV).—The acid (5 g.) was heated with 50 c.c. of 20% potassium hydroxide solution in a sealed tube at 100° for 18 hours, in another experiment the solution was boiled for a week. The acid was recovered unchanged in both cases.

Unsuccessful attempts were made to prepare the hydroxy anhydride or the anhydride by boiling the acid with acetyl chloride or with acetic anhydride, in both the cases the original acid was recovered unchanged.

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The Alkaloids of *Holarrhena Antidysenterica*. Part II. Two further New Alkaloids from the Bark and the Seeds of Indian *Holarrhena* and their Constitutional Relationship to Conessine.

By Salimuzzaman Siddiqui.

In collaboration with P P. Pillay, the author communicated in Part I (*J. Indian Chem. Soc*, 1932, 9, 553) the isolation of one non-oxygenous and two oxygenous new bases from the bark of Indian *Holarrhena* and characterised them in some detail. The present paper deals with the isolation and characterisation of of two further new alkaloids, named *iso*conessimine ($C_{23}H_{38}N_2$) and conimine ($C_{22}H_{36}N_2$), initially from the seeds and subsequently from a fresh working of the bark of Indian *Holarrhena*. It further embodies the results of investigation into the relationship of the non-oxygenous bases to conessine.

Out of the three new bases from the bark communicated in Part I (*loc. cit.*) only holarrhimine and conessimine could so far be isolated from the seeds. The yields of the new bases approximately amounted to 0·02 %, but as their complete purification entailed an enormous loss of material, the actual quantities of the bases present in the plant are likely to be far in excess of these yields. The nomenclature of the secondary bases is intended to mark their relationship to conessine and is based on the assumption that the difference between conessimine and *iso*conessimine depends on whether the active H is attached to the one or the other of the two basic nitrogen atoms, and that in conimine one active H is attached to each of the two nitrogen atoms. This assumption is fairly justified by the results of methylation of the secondary bases but a fuller investigation into the problem is in progress.

The isolation of these alkaloids was based on the differences of their basic strength and the separation of the secondary bases as petroleum ether insoluble carbonates. Thus the more strongly basic disecondary base conimine is precipitated as a carbonate on passing carbon dioxide through a moist ethyl acetate solution of the secondary bases, while conessimine and *iso*conessimine remain in solution and are separated from each other by means of fractional crystallisation from ethyl acetate, in which *iso*conessimine is more soluble than conessimine. The main portion of *iso*conessimine, however, was isolated out of the fraction of tertiary bases from the final mother liquors of conessine hydrogen oxalate, by fractionally precipitating the bases from the aqueous solution of the crystalline hydrobromide with ammonia and caustic soda. Of the three fractions finally obtained by this process, the middle fraction crystallised almost completely from acetone, yielding a base melting at 85°. On repeated fractional crystallisation of this base from petroleum ether and acetone, the middle fraction finally yielded *iso*conessimine which melted at 92° and gave a large depression in its melting point on admixture with conessimine.

In view of the isolation of three crystalline bases from the mother liquors of conessine hydrogen oxalate by the above mentioned process (from the seeds), it becomes rather doubtful, if Haworth's *nor*conessine (*J. Chem. Soc.*, 1932, 631), which was isolated from a corresponding fraction of the alkaloids from the seeds and form an uncrystallisable liquid inspite of the high molecular formula $C_{23}H_{38}N_2$, could be rightly considered as a uniform product, particularly when the base from the oxalate was not subjected to a fractional distillation. Haworth himself states that it was not possible to get pure conessine oxalate merely by fractional crystallisation and it is open to doubt, if what was not possible in case of conessine oxalate was so in case of *nor*conessine oxalate.

The acetyl and benzoyl derivatives of conessimine were prepared as additional proofs of its secondary character, already indicated by its forming a nitroso derivative (*loc. cit.*). Its methylation to a ditertiary base presented special difficulty as the methyl iodide in various solvents and under varying conditions invariably added itself on to the tertiary N, yielding a product which combines in itself the characters of a secondary base and a quarternary methiodide. Thus it gave an unstable nitroso derivative and picrate, but the

base could not be liberated from its aqueous solution by caustic soda.

Failing this method of methylation, refluxing the base for a couple of hours with one mol. each of formic acid and formaldehyde at 100° was tried with success. The methyl base was obtained in a yield of 70% of theory, but rather against expectations it melted higher than conessimine and was proved to be conessine by the determination of the mixed melting point and optical activity. Following up this method of methylation both *iso*conessimine and conimine gave conessine in nearly theoretical yields, and the mixture of the petroleum ether soluble bases (from 2 kg. of the bark), left after the separation of conessine, gave on direct methylation a further yield of 0·4% conessine, the total yield of the base thus amounting to 0·8%

Nearly all the previous authors who have worked on conessine have noted that it forms a red solution on heating in solvents and have recommended as little heating as possible to avoid loss in the yield of the pure base. A certain amount of heating, however, is unavoidable in the process of isolation and it was found that the reddening of solution is reduced to a minimum if the solvents are distilled off in a current of carbon dioxide. In contrast to conessine the solutions of the corresponding secondary bases are much less inclined to turn red on heating. This observation is of interest, as a similar behaviour has been noted before in respect of the corresponding secondary and tertiary bases. Thus nicotine turns dark on standing while *nor*nicotine is fairly stable (Braun and Weissbach, *Ber.*, 1930, **63**, 2018). Also methyl anabasine is less stable than the corresponding *nor*-base anabasine (Orechoff and Norkino, *Ber.*, 1932, **65**, 725).

At the close of the present investigations, Bertho, Schukmann and Schönberger, (*Ber*, 1933, **66**, 786) recorded the isolation of three new bases from the kurchi bark, namely conessidine ($C_{21}H_{32}N_2$), m. p. 128° conkurchine ($C_{20}H_{32}N_2$), m. p. 153° and kurchenine ($C_{21}H_{32}O_2N_2$), m. p. 335-36°. In view of the number of their carbon atoms and *N*-methyl groups, as well as their melting points and optical activity (*vide* Table), *iso*conessimine and conimine are quite distinct from conessidine and conkurchine, which may possibly be isolated later from the final mother liquors, which are under investigation.

Table showing the non-oxygenous bases from the bark and the seeds of *Holarrhena antidysenterica.*

Alkaloid.	Formula.	M. p.	$[\alpha]_D$.	No. of N-CH_3 groups.	Active H after Zerevitinoff.	Author.
Kurchine	$C_{23}H_{38}N_2$	75°	+6·4° in absolute alcohol, −7·57 in chloroform	Not mentioned	...	Ghosh & Ghosh
*nor*Conessine	$C_{23}H_{38}N_2$	liquid	+6·7°	8	...	Haworth
Conessine	$C_{24}H_{40}N_2$	126°	+27·6° in absolute alcohol	8	...	As purified by Siddiqui and Pillay
Conessimine	$C_{23}H_{38}N_2$	100°	−22·5°	2	1	Siddiqui & Pillay
*iso*Conessimine	$C_{23}H_{38}N_2$	92°	+30°	2	1	Present author
Conimine	$C_{22}H_{36}N_2$	134°	−30°	1	2	,, ,,
Conessidine	$C_{21}H_{32}N_2$	123°	−52·2° in chloroform	1	Not mentioned	Bertho, Schuckmann, & Schönberger
Conkurchine	$C_{20}H_{32}N_2$	153°	−67·4° in 96 % alcohol	0	Do	,,

EXPERIMENTAL.

Isolation of the bases from the seeds.—The well powdered seeds (20 kg.) were macerated with a mixture of alcohol and concentrated ammonia (9:1) and then heated to boiling for about ½ hour. After the temperature has come down to about 40°, 10% alcoholic potash was added and well stirred and the first percolate drawn out after a week. Six further percolations were subsequently made with cold 5% alcoholic potash and the combined percolates acidified with acetic acid and freed of the solvent in *vacuo* below 40°. The pasty greenish brown residue was extracted with light petroleum till free from the oil, then made strongly alkaline with caustic soda and extracted with ether and finally chloroform. The ether and chloroform extracts yielded, through the hydrochloride, 180 g. of the total alkaloid as a light reddish yellow treacle. Working on the basis

of the method outlined in the introduction, 40 g. of conessine melting at 123-24° and 2·5 g. of *iso*conessimine m.p. 92°, were obtained from the non-carbonate-forming fraction, while conimine, m.p. 134° and 2 g. of *iso*conessimine m. p. 80-90° were obtained from the corbonate-forming fraction, after separating from the later the insoluble sulphates, which yielded 8 g. of holarrhimine, m. p. 183°, after the method given for its isolation in Part I. (*loc. cit.*)

Isolation of the bases from the bark.—Working up 30 kg. of freshly collected, dried bark after the method given in the last communication (*loc. cit.*) and using the process of separation of alkaloids worked out on the seeds, conessine (100 g., m p. 123-24° and 20 g. second crop, m. p. 120-21°, total yield, 0·4 %), and *iso*conessimine (2 g.) were obtained from the non-carbonate fraction and conessimine (15 g., 0·05 %), *iso*conessimine (10 g., 0·03%) and conimine (3 g., 0·01%) from the carbonate fraction. The sulphate group yielded 0·1 % of holarrhimine, traces of holarrhine, and the crystalline residual alkaloid from the mother liquors of holarrhimine, which slowly melt from 150° to 173° (yield 0·05 %). The melting points of the different bases from the bark were identical with those of the corresponding bases from the seeds, the respecive mixed m. p. showing no depression. The values of the optical activity of the corresponding bases were also identical within limits of error.

Characterisation of Alkaloids, their Salts and Derivatives.

iso*Conessimine.*

iso*Conessimine* crystallises from its concentrated solutions in petroleum ether or more easily from acetone in puffs of white needles or clusters of well formed broad needles, which in contrast to conessine do not change into plates on stirring. It melts at 92° (corr.) and its solubility in acetone is distinctly greater than that of conessine. It is readily soluble in all the other common organic solvents. In 1·00% solution in absolute alcohol it showed a rotation α_D^{31} = +30·0°. (Found: C, 80·4, H, 11·1; N, 8·1. $C_{23}H_{38}N_2$ requires C, 80·7; H, 11·1; N, 8·2 per cent). After Herzig and Meyer's method it showed the presence of 2 *N*-methyls. [Found: CH_3, 9·5. $C_{23}H_{38}N_2$ requires (for 2 *N*-CH_3) CH_3, 8·8 per cent].

After Zerevitinoff it showed the presence of 1 active H. [Found: H, 0·22; $C_{23}H_{38}N_2$ requires (for 1 active H), H, 0·29 %]. On

crystallisation from moist ethyl acetate the dihydrate of the base was obtained in aggregates of needles melting at 88-92°. (Found in air dried substance: C. 72·6; H, 11·1. $C_{23}H_{38}N_2,2H_2O$ requires C, 72·0; H, 11·1 per cent). *iso*Conessimine forms a carbonate on passing a vigorous current of moist CO_2 through its petroleum ether solution, but the carbonate is much less stable than either conessimine or conimine carbonate, and forms a sticky semi-solid mass. On exposure to air *iso*conessimine absorbs moisture and CO_2 from the atmosphere and then melts from 80 to 85°, but the original melting point is restored on complete drying in vacuum over chloroform. A similar behaviour has also been noted in case of conessimine.

iso*Conessimine hydrochloride* was prepared by bringing together the components in ethereal solution and crystallised from a little alcohol and acetone. It forms a white crystalline powder, m. p. 335° and is exceedingly soluble in alcohol and water. (Found: Cl, 16·9. $C_{23}H_{38}N_2$, 2 HCl requires Cl, 17·1 per cent).

iso*Conessimine chloroplatinate*, prepared by adding 5% platinic chloride solution to an aqueous solution of conedine hydrochloride, formed a dull orange coloured semi-crystalline powder, which begins to darken at 270°, melts with decomposition at 285° and is insoluble in alcohol and water. (Found: Pt, 26·0. $C_{23}H_{38}N_2$, 2HCl, $PtCl_4$ requires Pt, 25·9 per cent).

iso*Conessimine hydroiodide* was obtained by adding potassium iodide solution to an aqueous solution of the hydrochloride as long white needles, melting at 316°. In contrast to the hydroiodide of conessine and its *nor*-bases, conedine hydroiodide is quite readily soluble in cold water.

iso*Conessimine picrate* was obtained by adding an aqueous solution of picric acid to an aqueous solution of the hydrochloride. It forms clusters of lemon yellow rectangular plates and broad needles from dilute alcohol which give off water at 110°, shrink down at 160° and melt with decomposition at 198-200°. It is difficulty soluble in hot alcohol and water.

iso*Conessimine hydrobromide* was prepared by adding an excess of potassium bromide to an aqueous solution of the hydrochloride. It separates out in long silky needles and planks, which are very soluble in water and a little less so in alcohol, m.p. 344° (decomp.).

Methyl iso*conessimine*: *Conessine*.—0·28 G. of *iso*conessimine was refluxed on the water-bath for an hour with 1·2 mols. each of formaldehyde (40 % solution) and formic acid (25 % solution). On

working up the reaction product as in case of the conessimine 0·18 g. (60 % of theory) of conessine (m.p. 125°) was obtained. (Found: C, 80·75; H, 11·27; N, 7·87. $C_{24}H_{40}N_2$ requires C, 80·99; H, 11·3; N, 7·87 per cent).

Conimine.

Conimine crystallises from its fairly concentrated solution in ether, petroleum ether, ethyl acetate or acetone in clusters and stars of needles, m.p. 130° (corr.). It is comparatively less soluble in all these solvents than conessimine. Its rotation in 1% absolute alcoholic solution was $\alpha_D^{25} = -80°$. (Found: C, 79·9; H. 11·0; N, 8·7. $C_{22}H_{36}N_2$ requires C, 80·5; H, 11·0; N, 8·5 per cent). It crystallises from moist ethyl acetate as a hydrate, m.p. 130°. (Found: H_2O, 9·9. $C_{22}H_{36}N_2$, 2 H_2O requires H_2O, 9·89 per cent). The dehydrated base showed the presence of two active H after the method of Zerevitinoff. [Found: H, 0·545. $C_{22}H_{36}N_2$ requires (for 2 active H) H, 0·609 per cent] and of only one *N*-CH_3, after the method of Herzig and Meyer. [Found: CH_3, 6·1. $C_{22}H_{36}N_2$ requires (for 1 *N*-CH_3) CH_3, 4·6 per cent].

Conimine hydrochloride was obtained by adding ethereal HCl to an ethereal solution of the base. Crystallised from a little methyl alcohol and acetone it forms nearly colourless aggregates of needles, m.p. 318-20° (decomp.) and is easily soluble in alcohol and water.

Conimine chloroplatinate was prepared by adding an aqueous solution of 5% platinic chloride to an aqueous solution of the hydrochloride. It forms a light orange coloured powder, m.p. 296-98° (decomp.) and is very sparingly soluble in hot alcohol or water. (Found: Pt, 26·36, 26·58. $C_{22}H_{36}N_2$, 2 HCl, $PtCl_4$ requires Pt, 26·47 per cent).

Conimine picrate was prepared by adding aqueous picric acid to the aqueous solution of the base in dilute hydrochloric acid and crystallising the semisolid precipitate from hot water, when it forms clusters of brilliant yellow prismatic rods, which shrink at 134° and melt at 140-41°. It is very sparingly soluble in hot alcohol and water.

Conimine hydroiodide was obtaiaed by adding a concentrated solution of potassium iodide to a solution of the base in dilute hydrochloric acid as a semi-solid precipitate which soon turns crystalline. It crystallises from water in white prismatic rods, m.p. 293°. It is fairly soluble in alcohol, less soluble in water.

Dimethylconimine : *Conessine*.—On refluxing 1 g. of conimine with 2·2 mol. each of 40 % formaldehyde and formic acid (25%) at 100° for 2 hours and working up the resultant product as in the case of conessimine, 0·07 g. of conessine was obtained (yield 66%). It melted at 125-26° and gave no depression of the melting point on admixture with pure conessine.

Conessimine.

Benzoyl conessimine.—On adding an ethereal solution of benzoyl chloride to an ethereal solution of the base benzoyl conessimine hydrochloride was obtained in nearly theoretical yield as a white crystalline powder which began to soften at 233°, melted at 348° (decomp.) and was easily soluble in water. The base from the hydrochloride was treated with moist carbon dioxide in petroleum ether solution to remove any traces of the unreacted secondary base, dried over potassium carbonate and taken up after removal of the solvent in a little acetone, from which it crystallised in elongated prismatic plates, which shrink at 110°, soften at 115° and melt completely at 121°. (Found: C, 79·4; H, 9·6. $C_{23}H_{37}N_2{\cdot}CO{\cdot}C_6H_5$ requires C, 80·2; H, 9·8 per cent).

Acetyl conessimine, prepared with acetyl chloride in exactly the same manner as the benzoyl base, formed a pale yellow uncrystallisable treacle. The hydrochloride of the base, as obtained directly from conessimine and acetyl chloride or prepared from the treacly acetyl base, had exactly the same m.p. 278-80° and was easily soluble in alcohol and water. (Found: Cl, 9·4. $C_{23}H_{37}N_2{\cdot}$ $CO{\cdot}CH_3$, HCl requires Cl, 8·6 per cent).

The chloroplatinate of the acetylated base, obtained by adding an aqueous solution of platinic chloride to an aqueous solution of the hydrochloride, formed a buff coloured powder which shrinks with darkening at 230° and melts at 254-56° (decomp.). The platinum value found for it indicates a double salt of the type (B, HCl) $1\frac{1}{2}$ $PtCl_4$. [Found: Pt, 20·6, 20·8. ($C_{23}H_{37}N_2{\cdot}CO{\cdot}CH_3$, HCl), $1\frac{1}{2}$ $PtCl_4$ requires Pt, 20·2 per cent].

Methyl conessimine : *Conessine*.—0·85 G of the base was refluxed at 100° for 3 hours with 1·2 mol. each of formaldehyde (40%) and formic acid (25%) till the carbon dioxide evolution was completely stopped. The base from the reaction mixture was treated with moist carbon dioxide in petroleum ether solution to remove traces of un-

reacted base and dried over potassium carbonate. On removing the solvent from the filtrate and crystallising the residue from acetone, 0·3 g. of crystals, m.p. 123-24° and further 0·3 g. melting at 121-22° were obtained. The base melting at 123-24° melted at 125-26° on admixture with pure conessine of m.p. 126° and showed a rotation in 2·016 % solution in absolute alcohol, $\alpha_D^{34} = +25 \cdot 8°$ as against +27·6° noted by the author for pure conessine.

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Halogenation. Part VIII. Bromination and Iodination of Monochlorotoluenes.

By Phuldeo Sahay-Varma and Vishwanath Sahay.

The action of bromine on chlorotoluenes has been studied before (Leonard, *J. Chem. Soc.*, 1916, **109**, 570; Jackson and Field, *J. Amer. Chem. Soc.*, 1879, **1**, 162). Cohen and Smithells studied the action of bromine on *o*-, *m*-, and *p*-chlorotoluenes in presence of amalgamated aluminium and obtained several isomeric chlorobromotoluenes (*J. Chem. Soc.*, 1914, **105**, 1911). Other chlorobromotoluenes have been obtained mostly by indirect methods. Direct iodination of chlorotoluenes does not seem to have been studied before; most of the chloroiodotoluenes have been obtained by indirect methods only.

We have brominated *o*-, *m*- and *p*-chlorotoluenes in presence of acetic acid, nitric acid or sulphuric acid. *o*-Chlorotoluene yields 2-chloro-5-bromotoluene, while *m*-chlorotoluene yields 3-chloro-4-bromotoluene and 3-chloro-6-bromotoluene in the proportion of about 8:1. With *p*-chlorotoluene, however, *p*-chlorobenzal bromide is obtained.

o-Chlorotoluene and *m*-chlorotoluene have been iodinated in presence of sodium nitrite and fuming sulphuric acid or a mixture of nitrosulphonic and fuming nitric acid and yielded 2-chloro-5-iodotoluene and 3-chloro-6-iodotoluene respectively. *p*-Chlorotoluene is not iodinated under these conditions.

Experimental.

o- or *m*-Chlorotoluene (10 c.c.) and bromine (6·5 c.c.) were heated together on a water-bath with a reflux condenser with 16 c.c. of acetic acid, 4 c.c. of strong nitric acid or 2 c.c. of fuming nitric or fuming sulphuric acid were added about ½ c.c. at a time at an interval of 10 minutes from the top of the condenser. After heating for 2-4 hours, the product of the reaction was washed with a dilute solution of sodium carbonate and the dried product distilled under

reduced pressure, when *o*-chlorotoluene distilled at 83°/12 mm and 2-chloro-5-bromotoluene at 90-98°/12 mm. Acetic acid and nitric acid yield about 4·8 to 5·5 c.c. of the chloro-bromo product, fuming sulphuric acid gives lower yield. With acetic acid the best yield is at the boiling point of chlorotoluenes.

Working in the same way with the same quantities, *m*-chlorotoluene yields about 5 c.c. of 3-chloro-6-bromotoluene (b. p. 90°-98°/12 mm.) and 1·5 c.c. of 3-chloro-6-bromotoluene (b. p. 120-25°/15 mm).

o-Chlorotoluene and iodine (5 g. each) were dissolved in acetic acid (20 c c.) and to this solution 2 c.c. of strong or fuming nitric acid or 1 c.c. of nitrosulphonic acid mixture was added (0 2 c.c. at a time) from the top of the condenser, and the mixture heated on a water-bath for 4 hours. In one experiment sodium nitrite (5 g.) and fuming sulphuric acid (7 c.c.) were added to the acetic acid solution. The yield of 2-chloro-5-iodotoluene is between 3 to 4 c.c. *m*-Chlorotoluene treated in the same way yielded *m*-chloro-6-iodotoluene (4 c.c.).

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Further Studies on the Chemical Behaviour of Vitamin B_2.

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Researches on the chemistry of vitamin B_2, which have been reported earlier (Guha, *Biochem. J.*, 1931, **25**, 945 ; Guha and Chakravorty, *Ind. J. Med. Res.*, 1933, **21**, 211), have shown that vitamin B_2 is chemically very different from vitamin B_1. Whereas vitamin B_1 behaved like a fairly strong base in electrolysis experiments (Birch and Guha, *Biochem. J.*, 1931, **25**, 1391) vitamin B_2 had obviously no basic properties (Guha, *loc. cit.*). It was observed that vitamin B_2 was precipitated or carried down by several metallic precipitants like lead acetate and silver nitrate. Some further investigations on the chemical behaviour of vitamin B_2 are reported in the present communication. Although it was found earlier by most workers (Narayanan and Drummond, *Biochem. J.*, 1931, **24**, 19 ; Salmon, Guerrant and Hays, *J. Biol. Chem.*, 1928, **80**, 91) that the vitamin was efficiently adsorbed but not easily eluted, we have recently succeeded in eluting the vitamin by means of suitable solvents. It may be mentioned that in view of the recent work on the relative instability of the vitamin in certain preparations to heat and alkali (Guha and Chakravorty, *loc. cit.*), procedures involving any heat treatment with alkali have been avoided in this work. The biological technique followed has been the same as described before (Guha and Chakravorty, *loc. cit.*). During the progress of this work Kuhn, György and Wagner-Jauregg (*Ber.*, 1933, **66B**, 1034) reported that vitamin B_2 belonged to a new class of natural pigments for which the term "flavin" has been employed. Only subsequent research can determine the correctness of Kuhn's contention (*cf.* also Ellinger and Koschara, *Ber.*, 1933, **66 B**, 808). Our results in many cases agree with those of Kuhn.

EXPERIMENTAL.

The following results were obtained chiefly with ox and buffalo liver and kidney extracts, which had been found to be very potent sources of vitamin B_2 (Guha, *loc. cit.* ; Guha and Chakravorty, *loc. cit.*).

The technique for the assay of the vitamin in different fractions was essentially the same as described before (Guha and Chakravorty,

loc. cit.). We have used the unit, previously defined (Guha and Chakravorty, *loc. cit.*), which is very similar to that proposed earlier by Bourquin and Sherman (*J. Amer. Chem. Soc.*, 1931, **53**, 3501).

From earlier observations (Guha, *loc. cit.*) it was known that vitamin B_2 could be adsorbed by charcoal although elution could not be effected. It was thought that the adsorption might be optimum at a specific hydrogen ion concentration and accordingly the following observations were made.

Effect of pH *on Adsorption of Vitamin B_2 on Charcoal.*

TABLE I.

Samples No.	Adsorption at diff. pH.	No. of rat.	Equiv. daily doses.	Average weekly growth.
O.L. (158) Glacial HAc ext. of charcoal adsorbate	1·2	385	16 g.	10 g.
O.L. (160)	3·0	365	12	
O.L. (162)	5·0	364	12	3
O.L. (164)	7·0	366	8	4
O.L. (168)	9·0	378	8	−4
O.L. (170)	11·0	458	8	3
O.L. (157) Filtrate from adsorption	1·2	414	4·5	9
O.L. (159)	3·0	397	6	5·6
O.L. (161)	5·0	...	...	...
O.L. (163)	7·0	378	5·2	−1
O.L. (167)	9·0	378	5	−2
O.L. (169)	11·0	394	5	1
O.L. (153) Crude liver extract used in this set of experiments		396	1·76	17·3

Six lots of crude liver extract of 220 c.c. each (≡200 g. of fresh liver), obtained by boiling ox-liver (5760 g.) with distilled water (6500 c.c.) for 6 minutes, were respectively adjusted to pH 1·2, 3·0, 5·0, 7·0, 9·0 and 11·0. Each lot was then agitated with purified * Merck's

* 100 G. of charcoal were digested for 30 hours over a flame with 1 litre of 50% hydrochloric acid. The acid was decanted off and the charcoal was washed chloride-free with distilled water. This purified charcoal was used throughout the experiments.

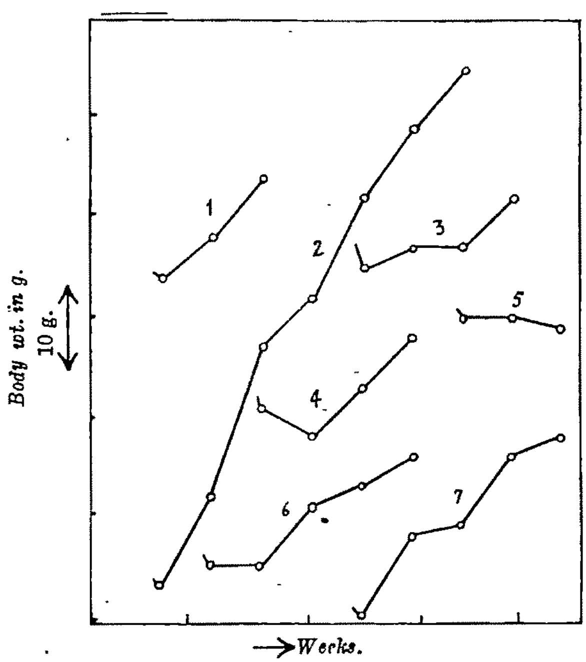
medicinal charcoal (3 g.) for ½ hour, filtered under suction and the filtrate was again agitated with charcoal (4 g.) for 15 minutes. The mixture was filtered on the same filter paper. The filtrate was stored in the refrigerator.

Each lot of the charcoal residue was ground up with glacial acetic acid (15-20 c. c.) and then digested for ½ hour on a boiling water-bath with a further amount of the acid. The total volume of acid used was 100 c. c. in each case. The mixture was then filtered hot under suction, the clear filtrate evaporated to dryness under reduced pressure and the residue taken up in warm water.

The extent of adsorption at the different hydrogen ion concentrations and the amounts of vitamin eluted are given in Table I. (*cf.* also Fig. 1).

It appears from the results in Table I that the adsorption of vitamin B_2 is not complete at any definite pH.

FIG. 1. (*cf.* Table I.)



Curve (1)	Rat No.	385 (female)	Fraction No.	O. L.	(158)
(2)		396 (male)	,,	,,	(153)
(3)		366 (,,)	,,	,,	(16[illegible])
(4)		364 (,,)	,,	,,	(162)
(5)		378 (female)	,,	,,	(168)
(6)		365 ,,	,,	,,	(160)
(7)		414 ,,	,,	,,	(157)

The Efficiency of Different Extractants in Eluting Vitamin B_2 from Charcoal Adsorbate.

880 C. c. O. L. (153), a crude liver-extract (≡800 g. of fresh liver) were brought to pH 7·0. 48 G. of purified Merck's medicinal charcoal were agitated with the extract for ½ hour. This was filtered under suction and the filtrate was kept in the refrigerator [O. L. (171)].

The finely ground charcoal residue was divided into four equal parts and treated as follows:

(*a*) *Elution with methyl alcohol.*—One portion (≡200 g. of fresh liver) of the residue was heated under reflux for 1 hour on a water-bath with methyl alcohol (250 c. c.) (Merck's "methanol purum"). The mixture was filtered hot under suction and the charcoal washed with a little methyl alcohol. The filtrate was almost colourless. The clear filtrate was evaporated to dryness *in vacuo* and the brown-red residue dissolved in warm water [O.L.(172)].

(*b*) *Elution with methyl alcohol and hydrochloric acid.*—Another portion (≡200 g. fresh liver) of the residue was similarly heated with methyl alcohol (250 c. c.) and concentrated HCl (5 c. c.), filtered hot under suction and the charcoal washed with a little methyl alcohol. The pale-brown filtrate was evaporated to dryness *in vacuo*. The dark brown pasty mass was dissolved in warm water [O L.(173)].

(*c*) *Elution with 1% hydrochloric acid.*—One portion (≡200 g. fresh liver) of the adsorbate was digested on a boiling water-bath for 45 minutes with 1% HCl (100 c.c.). The mixture was filtered hot under suction and the colourless filtrate was evaporated to dryness under reduced pressure. The dark-brown residue was taken up in warm water [O. L. (174)].

(*d*) *Elution with glacial acetic acid.*—One portion (≡200 g. fresh liver) of the residue was digested for 1 hour on a boiling water-bath with glacial acetic acid (100 c.c.). The mixture was filtered under suction and the pale brown filtrate evaporated to dryness *in vacuo*. The dark-brown residue was taken up in warm water [O. L.(175)].

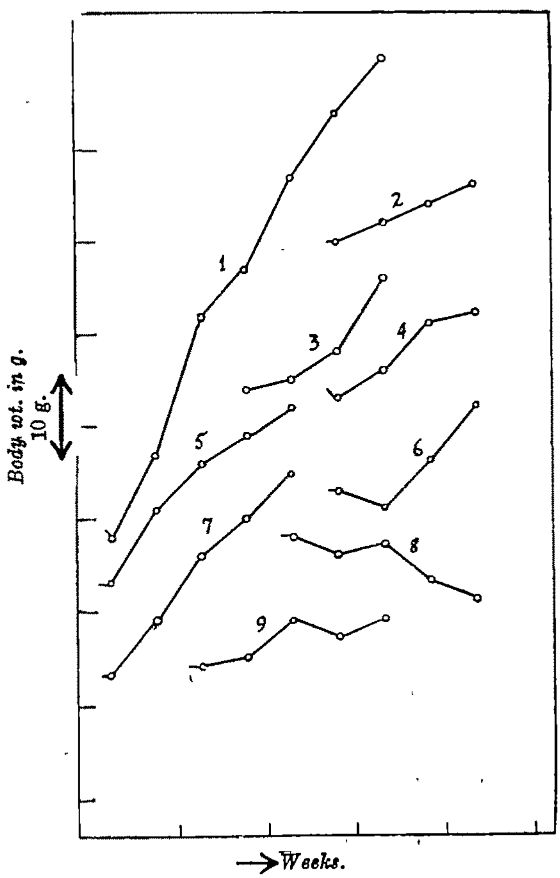
In another set of experiment 750 c.c. of O. L. (153), a crude aqueous extract of liver (≡681 g. of fresh liver) were brought to pH 7·0, agitated with Merck's purified medicinal charcoal (24 g.) for ½ hour and filtered under suction. The charcoal residue was divided into three portions and was treated as follows.

(*e*) *Elution with pyridine.*—A part of the charcoal residue (≡227 g. fresh liver) was digested at room temperature (29°) with

100 c.c. of pyridine, stirring continually for ½ hour. After filtering under suction, pyridine was distilled off *in vacuo* and the residue obtained was dissolved in warm water [O. L. (178)].

(*f*) *Elution with glacial acetic acid.*—A part of the charcoal residue (≡227 g. fresh liver) was digested on a boiling water-bath with glacial acetic acid (100 c.c.) for ½ hour. After removing charcoal by hot filtration, the clear yellow filtrate was evaporated *in vacuo* to dryness and the residue obtained was taken up in warm water [O.L. (179)].

FIG. 2 (*cf*. Table II).



Curve (1)	Rat. No. 396 (male)	Fraction	No. O. L.	(153)
(2)	312 („)	„	„	(126)
(3)	420 („)	„	„	(178)
(4)	593 (female)	„	„	(174)
(5)	390 („)	„	„	(178)
(6)	418 („)	„	„	(178)
(7)	419 („)	„	„	(179)
(8)	380 („)	„	„	(172)
(9)	399 („)	„	„	(171)

(g) *Elution with 25% pyridine.*—A portion of the charcoal was heated under reflux on a water-bath for 1½ hour with pyridine (260 c.c., 25%). After filtering hot under suction, the filtrate was evaporated to dryness *in vacuo*. The residue obtained was taken up in water [O. L. (126)].

(h) *Elution with conc.* HCl.—The experiment was carried out on a fresh lot of liver extract. 220 C.c. of O. L. (158) (≡200 g. ox-liver) were brought to pH 7·0 and agitated with purified charcoal (8 g.) for ½ hour and filtered under suction. The charcoal residue was ground up with concentrated HCl (10 c.c.) and then with 80 c.c. of water. This was boiled over a flame for 1-2 minutes and filtered hot under suction. The colourless dark filtrate was evaporated to dryness under reduced pressure. The residue was taken up in water [O. L. (189)].

Table II summarises the results obtained (*cf.* Fig. 2). Methyl alcohol with hydrochloric acid appears to be the most efficient agent for the elution of the vitamin, while methyl alcohol by itself could not extract vitamin B_2. Other extractants have varying capacities to elute the vitamin.

TABLE II.

Samples No.	Efficiency of different elutants. Descriptions.	No. of rat.	Equivalent daily dose.	Average weekly growth.
O. L. (171)	Filtrate after charcoal ad--sorption for elution expts.	399	5 g.	2·5 g.
O. L. (172)	Elution with MeOH	380	16	−3
O. L. (173)	,, ,, MeOH + HCl	390	8	11·5
O. L. (174)	,, ,, 1% HCl	398	8	6
O. L. (175)	,, ,, glacial acetic acid	459	10	6
O. L. (178)	,, ,, absolute pyridine (digestion)	418	9	6
,, ,,	,, ,, ,, ,,	420	18·6	16
O. L. (179)	,, glacial acetic acid	419	9	7
O. L. (180)	,, 1% ,, ,,	417	9·8	−2
O. L. (126)	,, ,, 25% pyridine refluxing	312	8	4
O. L. (158)	Crude liver extract used in this set of experiments	396	1·76	17·8
O. L. (189)	Elution with conc. HCl	391	13	2

Further Adsorption Experiments.

Vitamin B_2 has been reported to be adsorbed by various substances such as charcoal (Guha, *loc. cit.*), fuller's earth (Narayyanan and Drummond, *loc. cit.*) etc. In order to investigate the optimum conditions for adsorption and elution the following experiments were carried out.

(*a*) *Adsorption with fuller's earth.*—140 C.c. of B. L. (7), a crude aqueous extract of buffalo-liver (≡140 g. of fresh liver) were found to be at pH 5·0. The extract was stirred with 5 g. of Merck's fuller's earth for 15 minutes and filtered. The filtrate was tested for activity [B.L. (10)].

The fuller's earth residue was triturated with concentrated hydrochloric acid (10 c.c.) whereupon some evolution of CO_2 took place. This was then diluted to 75 c.c and boiled over an open flame for 2 minutes. The extracted residue was separated by filtration and the yellow filtrate was evaporated to dryness *in vacuo*. The residue, thus obtained, was taken up in warm water, neutralised and the precipitate obtained at that stage removed and the orange-red filtrate tested for activity [B. L. (18)].

In another experiment 100 c.c. of O.L. (68), a crude aqueous ox-liver extract (≡110 g. fresh liver) were adjusted to pH 4·5 and stirred with Merck's Fuller's earth (5 g.) for 20 minutes and filtered under suction. The filtrate was tested [O. L. 77)].

The residue was dried in the steam oven at 50° and powdered. The powder was stored at $-1°$ for 15 days and then tested for activity. The earth was suspended in water and tested [O. L. (81)].

(*b*) *Adsorption with charcoal and elution with* HCl.—140 C.c. of B.L. (7), a crude aqueous extract of buffalo-liver, (≡100 g. fresh liver) were agitated with purified Merck's medicinal charcoal (5 g) for 15 minutes. After separating the charcoal residue, the filtrate [B L. (11)] was tested for any vitamin left after adsorption.

The charcoal residue was boiled over a flame with water (50 c.c.) and concentrated hydrochloric acid (6 c.c.) for 3-4 minutes. The extracted residue was separated and the filtrate evaporated to dryness *in vacuo*. The residue obtained was taken up in water [B.L (14)].

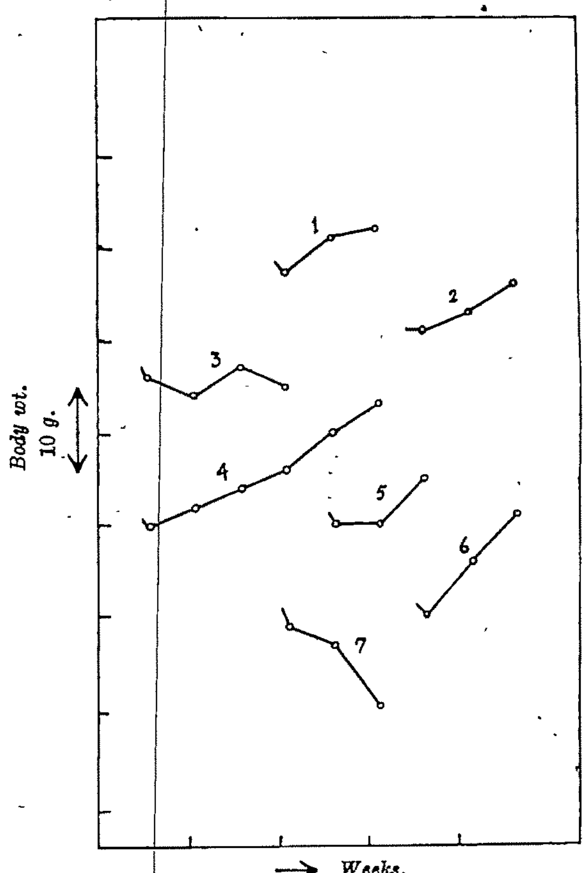
The extracted charcoal residue [B.L. (15)] was also tested for residual vitamin activity.

(*c*) *Adsorption with silica gel.*—200 C.c. of O. K. (11), a crude aqueous extract of ox-kidney, (≡80 g. of fresh kidney) were treated

with 10 g. of silica gel for 10-12 minutes and the silica residue separated by filtration under suction. The pale yellowish filtrate was numbered O.K. (13).

The silica residue was boiled with concentrated hydrochloric acid (200 c.c.) (large excess) and water (50 c.c.) over an open flame for 5 minutes and filterted under suction. The clear pale yellow filtrate was evaporated to dryness *in vacuo*. The dark brown residue was taken up in warm water. O.K. (14).

FIG. 8 (*cf.* TABLE III).



Curve (1) Rat. No. 114 (female) Fraction No. B.L. (14)
(2) ,, 140 (male) ,, O.K. (14)
(3) ,, 274 (,,) ,, O.L. (81)
(4) ,, 306 (,,) ,, O.L. (77)
(5) ,, 85 (,,) ,, B.L. (11)
(6) ,, 89 (female) ,, B.L. (14)
(7) ,, 90 (male) ,, B.L. (15

Silica-gel appears to adsorb vitamin B_2 efficiently and elution could be effected by boiling with strong hydrochloric acid.

(*d*) *Adsorption with barium sulphate.*—35 C.c. of O.L. (88), an active extract which was prepared by a method similar to that employed for O.L. (47), (≡785 g. fresh liver), were brought to p_H 9·0, by adding saturated baryta (25 c.c.) whereupon a small amount of precipitate was formed. A few drops of concentrated H_2SO_4 were added without removing the precipitate and the p_H was found to have come down to 6·0. The precipitate was allowed to settle overnight in the cold store. The barium precipitate was removed by centrifugation. The centrifugate was numbered O.L. (44).

The precipitate was boiled up for a minute with concentrated hydrochloric acid (8 c.c.) and 4 drops of concentrated H_2SO_4, diluted with water (15 c.c.). The residue was removed and the filtrate partly neutralised by 20% NaOH. A dark brown precipitate, which came down at this stage, was removed by centrifugation. The dark brown centrifugate was called O. L. (45).

The vitamin could not be found either in the filtrate or in the residue.

TABLE III.

No. of Samples.	Description	No. of Rat.	Equivalent daily dose.	Average weekly growth.
B. L. (10)	Filtrate from F. E. adsorption at p_H 5·0	109	4·2 g.	1·8 g.
B. L. (13)	HCl-ext. of F. E. adsorbate	84	4	−5
O. L. (77)	Filtrate from F. E. adsorption at p_H 4·5	306	5·8	4·8
O. L. (81)	F. E. adsorbate, dried and stored in the cold	274	8·3	Inactive
B. L. (11)	Filtrate from charcoal adsorption at p_H 7·0	85	4	5
B. L. (14)	HCl-ext. of charcoal adsorbate	86	4	7
,, ,,	,, ,, ,,	89	4	11
,, ,,	,, ,, ,,	114	8	5
B. L. (15)	HCl extracted charcoal residue	90	4	−9
O. K. (13)	Filtrate from Si-gel adsorption	132	3·2	Inactive
O. K. (14)	HCl-extract of Si-gel adsorbate	140	4	6·5
O. L. (44)	Filtrate from $BaSO_4$ -pptn.	181	7·4	Inactive
O. L. (45)	HCl-extract of $BaSO_4$	180	18	Inactive

Fractionation Studies.

With a view to fractionating vitamin B_2 its behaviour to certain precipitants, both metallic and organic, was studied.

(*a*) *Precipitation with cupric acetate.*—280 C.c. of B.L. (7) a crude buffalo liver extract (≡200 g. of fresh liver), were treated with about 100 c.c. of saturated cupric acetate solution. A precipitate began to come down and precipitation was complete after boiling for about ½ min. The greenish precipitate was removed by filtration under suction.

The filtrate was completely freed from copper by passing H_2S and from the latter by heating the filtrate on a water-bath *in vacuo* [B.L. (8)].

The filtrate was active while no activity could be traced in the precipitate fraction.

(*b*) *Fractionation with mercuric chloride.*—10 C.c. of O. L. (47), an active extract of liver obtained after the silver-stage (≡470 g. of fresh ox liver), were treated with 0·5*N*-$HgCl_2$ solution (2·2 c.c.) whereupon a small amount of precipitate came down. After allowing the precipitate to settle in cold store, the precipitate (A) was removed by centrifugation. The clear filtrate was freed from mercury as sulphide (B) by passing H_2S and the latter was removed by evaporating the liquid to dryness in a vacuum desiccator over $CaCl_2$ and soda lime. The small residue thus obtained was taken up in warm water [O. L. (52)].

The microcrystalline precipitate (A), which was chocolate coloured, was decomposed by H_2S and the sulphide removed. The filtrate was evaporated to dryness in a vacuum desiccator over $CaCl_2$ and soda lime and the residue obtained was taken up in water [O.L. (54)].

The sulphide precipitate (B) was boiled for 2 minutes over a flame with HCl about 8 c.c. of 25%. After filtering hot under suction the clear filtrate was evaporated to dryness on a water-bath. The residue was extracted with warm water and the mixture was filtered hot. The clear yellowish filtrate was called O.L. (53).

In another set of experiments 15 c.c. of O.L. (59) were treated with about $HgCl_2$ solution (6 c. c. of 5·8 %). A slight opalescence took place. Without removing the precipitate H_2S was passed till mercury was completely precipitated. The precipitate (A) was separated by filtration and the lemon-yellow filtrate was evaporated to dryness in a vacuum desiccator over $CaCl_2$ and soda lime. The residue was then taken up in water. [O.L. (62)]

The HgS precipitate (A) was extracted with boiling 25% HCl (25 c.c.) and filtered hot. The extract was evaporated to dryness on the water-bath and the residue was taken up in warm water [O.L. (68)].

The action of $HgCl_2$ appears to be similar to that of barium inasmuch as no activity could be found either in the $HgCl_2$ precipitate or in the filtrate left.

(c) *Experiments with bromine.*—120 C.c. O.L. (18) (≡100 g. fresh ox liver) were shaken with 25 c.c. bromine. A flocculent precipitate came down and was removed by filtering under suction. The filtrate was red owing to excess of bromine being present. It was evaporated to dryness *in vacuo*, and the residue thus obtained was taken up in warm water [O.L. (20)].

It appears that vitamin B_2 is stable to bromine.

(d) *Experiments with silver nitrate after bromination.*—From a few preliminary experiments meant to ascertain whether vitamin B_2 came down with the silver precipitate fraction after bromination or it remained dissolved in the filtrate, it was found that vitamin B_2 associated itself with the AgBr precipitate in course of pecipitation. This observation is in agreement with the earlier work of Guha (*loc. cit.*).

A suitable means of elution of the vitamin from this precipitate having been found the following experiment was carried out.

Eight litres of crude liver extract (7,500 g. of fresh liver) were brominated by adding about 13 c.c. of bromine with vigorous shaking. After allowing the precipitate to settle, the clear reddish supernatant liquid was syphoned off.

The liquid was treated with about 250 c.c. of 50% $AgNO_3$ solution and was left overnight for allowing the precipitate to settle.

The silver precipitate (180 g.) obtained by syphoning off the clear supernatant liquid and by subsequent filtration, was ground up with concentrated hydrochloric acid (65 c.c.) and then diluted with about 500 c.c. of water. The mixture was boiled over an open flame for 6 minutes and filtered hot under suction.

The clear red filtrate was freed from the acid by evaporation to dryness *in vacuo*. The residue was dissolved in warm water and the opalescent liquid was left overnight in the refrigerator. A dark brown precipitate came down and was removed by filtration under suction. [O.L. (47)].

Solvent Fractionation Methods.

Attempts were made to concentrate vitamin B_2 by means of fractionation with solvents, as described in the following experiments.

(*a*) *Fractional precipitation with* EtOH.—70 C.c. of O. L. (47), a concentrate of vitamin B_2 from ox-liver (≡3281 g. of fresh liver), were evaporated to a small volume (10-12 c.c.) on a water-bath. On adding about 50 c.c. of absolute alcohol an immediate precipitation took place. After cooling down to 0°, the precipitate (A) was removed by centrifugation. The centrifugate, which was opalescent, was further treated by an equal volume (70—75 c.c.) of absolute alcohol, whereby further precipitation took place. The residue (B) was removed by centrifuging. The clear centrifugate, after adding some more alcohol, was left in the refrigerator and after 6 days precipitate (C) appeared and was separated by centrifugation. The clear centrifugate was freed from alcohol by evaporating to dryness *in vacuo* and the black-brown residue obtained was taken up in warm water. This did not dissolve entirely. [O.L. (50).]

The precipitates (A) and (B) were mixed together and dried in a vacuum desiccator over $CaCl_2$ and soda lime. The dried residue, which was reddish brown, did not dissolve in water. This was fed in aqueous suspension [O.L. (48)].

The precipitate (C) was also dried in a vacuum desiccator over $CaCl_2$ and soda lime. The dried residue was a light yellowish brown powder which dissolved in water giving a dark brown solution with green flourescence [O.L. (49)].

(*b*) *Precipitation with* MeOH.—25 C.c. of B.L. (55) (≡116 g. of fresh buffalo liver), were treated with methyl alcohol (50 c.c.) and left in the refrigerator. The precipitate formed was separated by filtration and dried and was found to be very hygroscopic. The dried residue could not be entirely dissolved in boiling water [B.L. (56)].

The filtrate was concentrated on a water-bath to remove methyl alcohol and was tested for vitamin B_2 activity. [B.L. (60).]

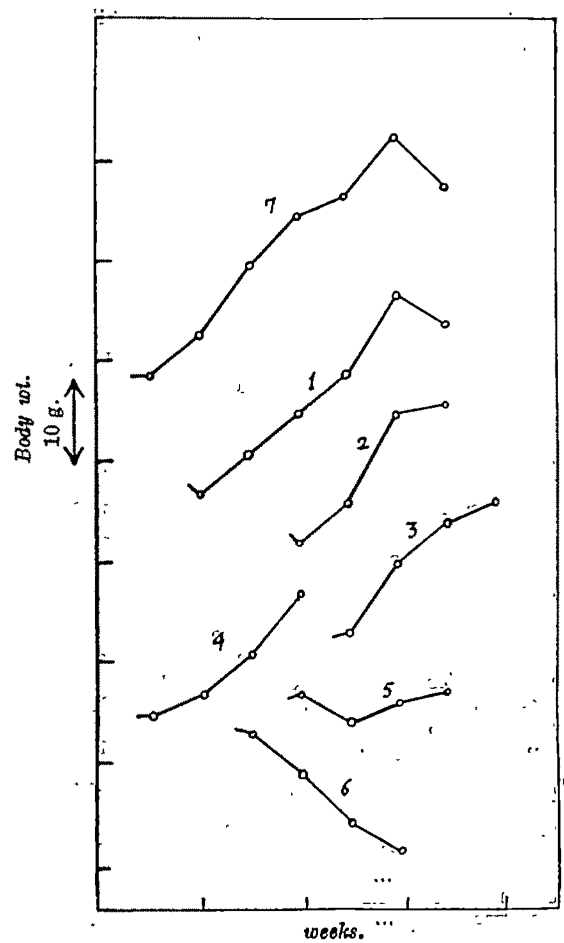
The methyl alcohol filtrate had no activity while the residue was active.

(*c*) *Precipitation with propyl alcohol*—20 C.c. of B.L. (55) (≡116 g. fresh buffalo liver) were treated with *n*-propyl alcohol (4 c.c.) and a gummy precipitate obtained. The clear supernatant liquid was removed by decantation and the washed residue was dried

in vacuum desiccator over $CaCl_2$ and soda-lime. The dried residue was taken up in hot water [B.L. (58)].

The washings and the supernatant liquid from the above fraction were combined and were freed from alcohol by evaporating to a small volume on a water-bath. The fraction was tested for activity. [B.L. (61)].

FIG. 4 (*cf.* TABLE IV)



Curve (1)	Rat. No.	183 (female)	Fraction No.	O.L. (47)
(2)	,,	175 (,,)	,,	,, (47)
(3)	,,	182 (male)	,,	,, (50)
(4)	,,	74 (female)	,,	B.L. (8)
(5)	,,	274 (male)	,,	O.L. (53)
(6)	,,	269 (,,)	,,	B.L. (61)
(7)	,,	194 (female)	,,	B.L. (55)

It is curious to note that no activity could be found either in the propyl alcohol filtrate or in the residue. No growth was observed even when both the residue and filtrate were fed together.

Testing Known Substances for Vitamin B_2 Activity.

Following substances were tested for vitamin B_2 activity with negative results. The daily dose is given in brackets.

Arabinose (1 mg.), xylose (1 mg.), galactose (1 mg.), arabinose + xylose (1 mg. each), arabinose + glactose (1 mg. each), irradiated adenine (5 mg.), irradiated guanine (5 mg.), cytosine (5g.).

TABLE IV.

Samples No.	Description.	No of Rat.	Eqiuv. daily dose	Average weekly growth.
B. L. (8)	Filtrate from $CuAc_2$ -pptn	94	10 g.	8 g.
O. L. (52)	Filtrate from $HgCl_2$ -pptn of O. L. (47)	269	18·8	1
O. L. (54)	Extract of $HgCl_2$ .ppt. ...	270	18·8	0
O. L. (58)	Extract of HgS obtained from O. L. (52)	274	14·1	0
O. L. (62)	Filtrate from $HgCl_2$-treated fraction	268	12·8	Inactive
O. L. (63)	HgS extract	273	19·8	Inactive
O. L. (20)	Br_2 treated liver extract ...	180	8	2·7
O. L. (47)	Ag extract after bromine treatment	175	14	9·3
,,	,, ,, ,, ,,	180	10	4·7
,,	,, ,, ,, ,,	183	10	12·5
O. L. (50)	Centrifugate after EtOH -pptn.	182	32·8	8·7
O. L. (48)	The first fraction precipitated by alcohol	186	32·8	8
O. L. (49)	The second ,, ,,	185	32·8	5·8
,,	,, ,,	178	16·4	2·7
B. L. (56)	Residue from MeOH-treated B.L. (55)	270	8·8	9·3
B. L. (60)	Filtrate from MeOH-treated B. L. (55)	268	9·8	Inactive
B. L. (58)	Residue from propyl alcohol fractionation	269	9·8	−3
B. L. (61)	Filtrate from propyl alcohol fractionation	269	14·5	Inactive
B. L. (61) } B. L. (58) }	Propyl alcohol residue and filtrate	269	7·25 of filtrate and 4·6 of residue	Inactive
B. L. (55)	Desiccated buffalo liver extract	194	2·9	7

Discussion.

The results described in this paper indicate that most metallic fractionations cause a very considerable loss of vitamin B_2 probably owing to adsorption on the surface of the various precipitates formed. Results obtained are better with methyl alcohol, although in solvent fractionation methods also a satisfactory recovery of activity is not usually possible. The adsorption experiments, if further pursued, are likely to give greater scope for successful concentration. Adsorption on charcoal and elution with methyl alcohol and hydrochloric acid constitute one of the most effective methods for concentration so far discovered.

The procedure, which has given consistently good results, consists of bromination (which causes no loss); adsorption with silver bromide and elution with hydrochloric acid, followed by adsorption methods.

It is not possible yet to postulate the nature of the vitamin B_2 molecule. Our experience indicates, that it is not at all so stable as it was originally supposed to be. The precipitation of the vitamin by silver nitrate and lead acetate (Guha, *loc. cit.*) might indicate either that the vitamin is acidic or that it is neutral and is adsorbed by the metallic precipitates formed. It has been pointed out before (Guha, *loc. cit.*) that it cannot be of the nature of a base.

The remarkable stability of the vitamin to bromine appears to indicate that the activity is not associated with any unsaturated linkage in the molecule.

Summary.

1. The adsorption of vitamin B_2 on charcoal at p_H 1·2, 3·0, 5·0. 7·0, 9·0. and 11·0 was studied. No high degree of specificity was observed at any of the above hydrogen ion concentrations under the stated conditions.

2. Methyl alcohol with HCl, absolute methyl alcohol, 1% HCl, glacial acetic acid, absolute pyridine, 25% pyridine and strong hydrochloric acid were tried to elute vitamin B_2 from the charcoal adsorbate. Methyl alcohol with hydrochloric acid and pyridine were found to be the most efficient of all the extractants used. Methyl alcohol by itself could not elute the vitamin.

3. Vitamin B_2 could be apparently adsorbed by fuller's earth, charcoal, silica gel and freshly precipitated barium sulphate. While the vitamin could be eluted from the charcoal and silica gel adsorbates, the methods employed were not found so suitable for the elution of the vitamin from fuller's earth or barium.

4. Bromine could neither precipitate nor destroy the vitamin to any appreciable extent. Silver either forms an insoluble compound with vitamin B_2 or silver bromide can adsorb it. The vitamin could not be concentrated by means of $HgCl_2$ or propyl alcohol. Ethyl alcohol can fractionally precipitate the vitamin. Methyl alcohol forms a precipitate which contains most of the activity.

5. Sugars like arabinose, xylose and galactose, administered singly or in combination with one another, could not replace vitamin B_2 in the diet. Irradiated adenine, guanine, cytosine and nucleic acid have no vitamin B_2 activity.

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Chemical Reactivity and Light Absorption. Part II.

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From considerations based on several chemical reactions, it was concluded in Part I of this series (*J. Indian Chem. Soc.*, 1934, 11, 38) that an increase in chemical reactivity of a molecule is associated with increased light absorption. The weakening of the binding forces of molecules, due to the presence of molecules of another substance, leads to an increase in the light absorption.

We have carried on further work on this subject and the results and conclusions are recorded in this paper. We have measured the light absorption of different reacting substances separately and in mixtures by photographing their absorption spectra with Hilger quartz spectrographs using a copper arc as the light source. The exposure for taking the photograph varied from 7—30 seconds. The amount of chemical change during the period of exposure was negligible and hence the products formed as the result of the chemical change from the reacting mixtures did not play any important part in affecting the light absorption. Moreover, in many cases, the light absorption by the resultants is less than those of the reacting substances.

Reactions involving Chlorine.

(*a*) *Chlorine and hydrogen.*—Some years ago Weigert and Kellermann (*Z. physikal. Chem.*, 1923, 107, 1) obtained some interesting results on the light absorption by a mixture of chlorine and hydrogen. They took a cinematograph exposure of a small cell filled with chlorine and hydrogen and illuminated by a spark discharge giving out intense light. As long as there was no chemical reaction between chlorine and hydrogen on illumination, a photograph of the cell, which appeared to be empty, was obtained on the film but when the reaction started and in the course of about 1/50 second, a cloud developed in the reaction mixture and the increased light absorption due to the occurrence of the cloud or the fog in the mixture of hydrogen and chlorine was recorded on the cinematograph film. This observation

of Weigert and Kellermann, which has been adduced by Bodenstein (*Trans. Faraday Soc.*, 1925, **21**, 532) and others as evidence of chain reactions, appears to us to be a case of the weakening of the binding forces of the chlorine molecules due to the presence of hydrogen and the consequent increase in light absorption by the system and supports our view that an increase in the chemical reactivity is associated with increased light absorption.

(*b*) *Oxalic acid and chlorine.*—This photochemical reaction has been investigated by Bhattacharya and Dhar (*J. Chim. phys*, 1929, **26**, 556). In absence of hydrochloric acid, the reaction is extremely rapid and hence the reaction has been studied in presence of hydrochloric acid, which was added to the chlorine water. Fig. 1 shows that the light absorption by a mixture of chlorine water and oxalic acid solution is greater than the absorptions by chlorine water and oxalic acid considered separately.

Moreover, we have shown that this reaction is appreciably accelerated by radiations of wave-lengths 5650, 7804 and 8500Å, although the limits of sensitised decomposition and photochemical dissociation for chlorine molecules are 5000 and 4780Å respectively. Hence in presence of oxalic acid, the decomposition of chlorine molecules is markedly sensitised and these molecules become reactive in radiations of wave lengths longer than the sensitised and the photochemical dissociation limits. Along with this increased reactivity of chlorine molecules, a marked increase of light absorption is also observed.

Reactions involving Bromine.

(*a*) *Potassium oxalate and bromine.*—Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 523) have shown that this reaction is appreciably accelerated by radiations of wave-lengths 7304 and 8500Å, although the limits of sensitised decomposition and photochemical dissociation for molecules of bromine are 6300 and 5100Å. Fig. 2 shows that the light absorption by a mixture of a solution of potassium oxalate and bromine water containing hydrochloric acid is greater than those of the two ingredients taken separately. Here again we find that the presence of an oxalate sensitises the decomposition of bromine molecules and makes them reactive in radiations of longer wave-lengths and the light absorption is markedly increased due to the weakening of the Br—Br linking.

(*b*) *Tartaric acid and bromine.*—Ghosh and collaborators (*J. Indian Chem. Soc.*, 1925, 2, 165; 1928, 5, 342, 361) studied this reaction carefully in radiations of wave-lengths 4500-4900Å and Bhattacharya and Dhar (*ibid.*, 1929, 6, 451) investigated the reaction between Rochelle salt and bromine in radiations of wave-length 7304Å, which markedly accelerate the reaction. The limits of sensitised decomposition and photochemical dissociation of bromine molecules are 6300 and 5100Å. Hence in presence of Rochelle salt, the dissociation of bromine molecules is markedly sensitised and and these molecules become reactive in radiations of wave-lengths longer than the sensitised and photochemical dissociation limits of bromine. Along with this increased reactivity of bromine molecules, a marked increase of light absorption is observed as will be evident from Fig. 3.

Reactions involving Iodine.

(*a*) *Potassium oxalate and iodine.*—It has been stated in Part I (*loc. cit.*) that in presence of an oxalate, the dissociation of iodine molecules is sensitised. Fig. 2 shows that the light absorption by a mixture of iodine and potassium oxalate solutions is much greater than those of iodine and oxalate considered separately.

(*b*) *Sodium formate and iodine.*—This reaction is also accelerated by radiations of wave-lengths 7304 and 8500Å, the limits of sensitised decomposition and photochemical dissociation for iodine molecules being 8050 and 4995Å respectively. Fig. 4 shows that the light absorption by a mixture of sodium formate and iodine is much greater than those of the reaction mixture considered separately.

(*c*) *Acetone and iodine* (in presence of HCl as a catalyst).—This reaction has been studied by Bhattacharya and Dhar (*cf.* Dhar, "Chemical Action of Light," 1931, p. 161) in radiations of different wave-lengths including 7304Å. It appears, therefore, that in presence of acetone, the photo-dissociation of iodine molecules is sensitised. It is clear from Fig. 5 that a mixture of aqueous acetone and iodine shows greater absorption than the two substances taken separately.

(*d*) *Ferrous sulphate and iodine.*—Bhattacharya and Dhar (*cf.* Dhar, "Chemical Action of Light," 1931, p. 162) investigated this reaction in radiations of wave-lengths 7304 and 8500Å and hence the photo-

dissociation of iodine molecules is sensitised by the presence of the reducing agent, ferrous sulphate. It will appear from Fig. 6 that the light absorption by a mixture of ferrous sulphate and iodine is appreciably greater than those of the two ingredients estimated separately.

(*e*) *Sodium nitrite and iodine.*—Bhattacharya and Dhar (*cf.* "Chemical Action of Light," p. 163) observed that this reaction is appreciably accelerated by radiations of wave-lengths 7304 and 8500Å. It appears that the presence of sodium nitrite sensitises the dissociation of iodine molecules. The light absorption by a mixture of sodium nitrite and iodine is much greater than the absorptions due to sodium nitrite and iodine taken individually (*cf.* Fig. 7).

(*f*) *Sodium tartrate and iodine.*—This reaction has been found to be accelerated by radiations of wave-lengths 7304 and 8500Å and hence it is believed that the presence of sodium tartrate sensitises the dissociation of iodine molecules. Fig. 8 shows that the light absorption by a mixture of sodium tartrate and iodine is much higher than that by sodium tartrate and iodine considered separately.

(*g*) *Sodium lactate and iodine.*—Radiations of wave-lengths 7304 and 8500Å accelerate the reaction between sodium lactate and iodine and thus in this case also, the dissociation of iodine molecules is made more easy due to the presence of the reducing agent, sodium lactate. The light absorption by a mixture of sodium lactate and iodine is greater than those by the two substances when observed separately (*cf.* Fig. 9).

(*h*) *Sodium malonate and iodine.*—This reaction also takes place at a greater speed in radiations of wave-lengths 7304 and 8500Å than in the dark and hence the presence of the reducing agent sodium malonate sensitises the dissociation of iodine molecules. A mixture of sodium malonate and iodine shows a greater light absorption than solutions of sodium malonate and iodine taken individually (*cf.* Fig. 10).

(*i*) *Sodium malate and iodine.*—Radiations of wave-lengths 7340Å accelerate this reaction and hence the presence of sodium malate makes the iodine molecules more reactive and this is also corroborated by the increased light absorption by the mixture than the two ingredients considered separately (*cf.* Fig 11).

(*j*) *Sodium citrate and iodine.*—The reaction takes place at a greater velocity in radiations of wave-length 7304Å than in the dark

and hence the dissociation of iodine molecules is sensitised by the presence of sodium citrate. Moreover, the absorption of light by a mixture of sodium citrate and iodine solution is much greater than that by sodium citrate and iodine considered separately (*cf.* Fig. 12).

(*k*) *Hydroxylamine hydrochloride and iodine.*—This reaction is accelerated by radiations of wave-lengths 7304 and 8500Å and hence due to the presence of hydroxylamine hydrochloride, the photo-dissociation of iodine is facilitated. Fig. 13 shows that the light absorption by a mixture of hydroxylamine hydrochloride and iodine is more pronounced than that by hydroxylamine hydrochloride and iodine taken separately.

(*l*) *Hydrazine sulphate and iodine.*—This reaction takes place in radiations of wave-lengths 7304 and 8500Å at a speed greater than that in the dark and hence the presence of hydrazine sulphate sensitises the photochemical decomposition of iodine molecules. Moreover, the light absorption by a mixture of hydrazine sulphate and iodine as shown in Fig. 14 is much greater than the absorptions of hydrazine sulphate and iodine considered separately.

(*m*) *Hypophosphorous acid and iodine.*—This reaction was studied in the dark by Steele (*J. Chem. Soc*, 1907, **91**, 1641). Dhar reported that it was light sensitive. The light absorption by the mixture in this case also is much greater than the absorptions due to iodine and hypophosphorous acid taken separately (*cf.* Fig 15).

(*n*) *Phosphorous acid and iodine*—The kinetics of this reaction have been investigated only in the dark by Steele (*ibid.*, 1908, **93**, 2203).

In this case also the light absorption by the mixture is appreciably greater than that caused by phosphorous acid and iodine considered separately (*cf.* Fig. 16). It is of interest to note that both the velocity of the reaction and the light absorption are greater in the reaction between hypophosphorous acid and iodine than in the reaction between phosphorous acid and iodine.

Reactions involving Chromic Acid.

(*a*) *Quinine sulphate and chromic acid.*—The oxidation of quinine sulphate by chromic acid has been investigated in different radiations as well as in the dark by several investigators, notably Goldberg (*Z. physikal. Chem.*, 1902, **41**, 1; *Z. wiss. Phot.*, 1906, **4**, 56), Luther

and Forbes (*J. Amer. Chem. Soc.*, 1909, **31**, 770), Dhar and collaborators (*J. Chem. Soc.*, 1917, **111**, 717; "Chemical Action of Light", 1931, p. 190), Forbes and co-workers (*J. Amer. Chem. Soc.*, 1923, **45**, 1891; 1933, **55**, 588). Both the reacting substances showed marked light absorption but the mixture absorbs more than the ingredients taken separately as will be evident from Fig 17.

(*b*) *Oxalic acid and chromic acid.*—This reaction has been investigated by Dhar and collaborators in the dark and in light. Fig. 17 shows that the light absorption by a mixture of oxalic acid and chromic acid is appreciably greater than that by oxalic acid and chromic acid considered separately.

(*c*) *Formic acid and chromic acid.*—This reaction has been studied by Dhar (*J. Chem. Soc.*, 1917, **111**, 707) in the dark It appears from Fig 17 that the light absorption by a mixture of formic acid and chromic acid is slightly greater than that by the two substances considered individually.

(*d*) *Hypophosphorous acid and chromic acid.*—Chromic acid is easily reduced to chromium salts in presence of hypophosphorous acid. Fig. 18 shows that the light absorption by a mixture of chromic acid and hypophosphorous acid is appreciably greater than that by chromic acid and hypophosphorous acid taken separately.

(*e*) *Phosphorous acid and chromic acid.*—This reaction was first studied by Dhar (*Ann. chim.*, 1919, *ix*, **11**, 130) in the dark. Fig. 18 shows that the light absorption by a mixture containing dilute solutions of phosphorous acid and chromic acid is greater than that by the two acids taken separately.

Reactions involving Potassium Permanganate.

(*a*) *Oxalic acid and potassium permanganate.*—This reaction has been investigated by several workers notably Harcourt and Esson (*Phil. Trans.*, 1866, **56**, 193), Skrabal (*Z. anorg. Chem.*, 1904, **42**, 1), Dhar and collaborators (*cf.* Dhar, "Chemical Action of Light," 1931, p. 196) in light as well as in the dark. Fig. 19 shows that the light absorption by a mixture of potassium permanganate and oxalic acid is much greater than that by potassium permanganate and oxalic acid considered separately.

(*b*) *Potassium permanganate and hydrochloric acid.*—It is well known that potassium permanganate reacts quite readily with hydro-

chloric acid. In this reaction also it is observed that the light absorption by a mixture of potassium permanganate and hydrochloric acid is appreciably greater than that by the two ingredients taken individually (*cf* Fig. 20).

Reactions involving Mercuric Chloride.

The increase in light absorption by different organic acids due to the presence of dilute solutions of mercuric chloride as observed by Ghosh and collaborators (*J. Indian Chem. Soc.*, 1928, **5**, 871) has already been considered in Part I of this series.

We have studied the cases of the reduction of mercuric chloride by phosphorous and hypophosphorous acids.

(*a*) *Mercuric chloride and hypophosphorous acid*.—The kinetics of this reaction have been investigated in the dark by Mitchell (*J. Chem. Soc.*, 1921, **119**, 1266). Fig. 21 shows that the light absorption by a mixture of mercuric chloride and hypophosphorous acid is appreciably greater than that by the two components taken separately,

(*b*) *Mercuric chloride and phosphorous acid.*—This reaction was first studied in the dark by Purkayastha and Dhar (*Z. anorg. Chem.*, 1922, **121**, 156). It will be evident from Fig. 22 that the light absorption by a mixture of mercuric chloride and phosphorous acid is greater than that by mercuric chloride and phosphorous acid considered individually.

Reactions involving Silver Nitrate.

(*a*) *Silver nitrate and sodium formate.*—Dhar (*J. Chem. Soc.*, 1917, **111**, 707) studied this reaction in the dark. Fig. 23 shows that the light absorption by a mixture of silver nitrate and sodium formate is appreciably greater than that by silver nitrate and sodium formate considered separately.

(*b*) *Silver nitrate and ferrous ammonium sulphate.*—Dhar, Datta, and Bhattacharya (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 299) and recently Roberts and Soper (*J. Chem. Soc.*, 1932, 2004) studied this reaction in the dark. The light absorption by a mixture of silver nitrate and ferrous ammonium sulphate is much greater than that by the two ingredients taken individually (*cf.* Fig. 24).

Reactions involving Hydrogen Peroxide.

(*a*) *Hydrogen peroxide and sodium thiosulphate.*—Abel (*Monatsh.*, 1907, **28**, 1239) has shown that hydrogen peroxide reacts with thiosulphate according to the equation

$$H_2O_2 + 2S_2O''_3 + 2H^{\cdot} = S_4O''_6 + 2H_2O.$$

Fig. 25 shows that the light absorption by a mixture of sodium thiosulphate and hydrogen peroxide is greater than that by the two constituents considered separately.

(*b*) *Hydrogen peroxide and glucose.*—Ghosh and Mukherji (*J. Indian Chem. Soc.*, 1929, **6**, 231) have studied the photo-oxidation of glucose and hydrogen peroxide in presence of tungstic acid sol. Fig. 26 shows that a mixture consisting of dilute solution of glucose and hydrogen peroxide absorbs light to a greater extent than the sum of the two ingredients considered separately.

It is well known that the oxidation of organic substances by hydrogen peroxide is accelerated by iron salts. Both ferrous and ferric salts are effective. We have observed that the addition of ferric chloride increases the light absorption by a mixture of hydrogen peroxide and an organic substance.

(*c*) *Hydrogen peroxide and potassium persulphate.*—This reaction was first studied by Friend (*J. Chem. Soc.*, 1906, **89**, 1096) in the dark. The light absorption by a mixture consisting of dilute solutions of hydrogen peroxide and potassium persulphate is appreciably greater than that by the two substances taken separately (*cf.* Fig. 27).

Reactions involving Oxygen.

Recently Dhar and Atma Ram (*J. Indian Chem. Soc.*, 1933, **10**, 287) have shown that organic substances like acetic acid, aminoacetic acid, glycerol, acetone, etc., are appreciably oxidised first to formaldehyde when they are exposed to air and light.

We have taken photographs of dilute solutions of acetic and aminoacetic acids before and after saturation of the solutions with oxygen in a large Hilger quartz spectrograph. Fig. 28 shows that the light absorption in the short ultraviolet region is appreciably greater with the solutions of acetic and aminoacetic acids when saturated with oxygen than in the absence of oxygen, which when dissolved in water shows slight absorption in the ultraviolet. From the figure it will be evident that the light absorption by a mixture of

acetic acid or aminoacetic acid and oxygen is slightly greater than that by the two ingredients considered separately.

As the beginning of molecular absorption of oxygen is in the region 2020Å, it is not possible to obtain more marked difference in absorption in the ultraviolet region with mixture of oxygen in an ordinary quartz spectrograph.

Iodic acid and oxalic acid.—The kinetics of this reaction in the dark and in light have been studied in this laboratory. Fig. 29 shows that the light absorption by a mixture of iodic and oxalic acids is greater than the absorptions of the two acids taken individually.

Hydrolysis of Cane Sugar.

The kinetics of this reaction has played an important rôle in the development of chemical dynamics and photochemistry. In publications from this laboratory it has been shown that this reaction is accelerated not only by ultraviolet light but also by radiations of wave-lengths 4725, 5650, 7304 and 8500Å.

It will be of interest to note from Fig. 30 that the light absorption by a mixture of hydrochloric acid and cane sugar is appreciably greater than that by cane sugar and hydrochloric acid taken separately.

DISCUSSION.

It has already been emphasised in Part I (*loc. cit.*) that the researches of Franck and Victor Henri show that whenever a molecule is rendered active and unstable, either by absorption of light or increase of temperature, and there is a loosening of the bond uniting the atoms, an increased light absorption by the molecules in this active condition is of common occurrence. Moreover, the experimental results brought forward in this and the previous papers are in support of the view that molecules can also be activated and there is consequent weakening of the binding forces by chemical agencies and this is evident by increased light absorption. Thus the binding forces of the halogen molecules, chlorine, bromine and iodine are weakened by the presence of reducing agents like hydrogen, sodium nitrite, ferrous sulphate, organic acids and their salts, etc., and in every case whenever there is the possibility of a chemical change between a halogen molecule and a reducing agent, and a weakening of the binding forces of the atoms in the halogen molecules takes place, it has always been observed that the light absorption by the mixture of the

two reacting substances is appreciably greater than the absorption due to the individual substances considered separately. Similar results have been obtained with other reacting substances. On the other hand, when there is no chemical change by mixing two substances, no increased light absorption is observed as is evident in the photographs taken with hydrochloric acid and oxalic acid singly or in mixture (*cf.* Fig. 31).

From the numerous cases cited in this paper it seems clear to us that if there is the possibility of the occurrence of a chemical change by mixing two or more substances, increased light absorption by the mixture is likely to be observed in those cases. We are of opinion that the increased light absorption by a mixture in comparison with those of the ingredients is likely to be a measure of the reactivity of a given mixture of two or more substances.

Over and above the important experimental results of Ghosh and collaborators (*loc. cit.*) on increased light absorption by mixtures already discussed from this point of view in Part I, the following observations by Ghosh and Chakravarti (*J. Indian Chem. Soc*, 1929, **6**, 823, 871) are of interest. These authors have observed a very marked increase in the extinction coefficient of mixtures containing a very dilute solution of copper sulphate and sodium sulphite in the red region. Moreover, it is well known that a copper salt is an excellent positive catalyst in the oxidation of sodium sulphite solution by oxygen. The above authors have also shown that the extinction coefficients of mixtures of Fehling's solution or Benedict's solution with reducing agents like glucose, glycerol, sodium formate, etc., are much greater in ultraviolet radiations of wave-lengths varying from 3750-2266Å than those of the ingredients considered separately. These observations are in support of our theory that the weakening of the binding forces of the molecules of cupric salts due to the presence of reducing agents leads to an increased light absorption. Recently Damon and Daniels (*J. Amer. Chem. Soc.*, 1933, 55, 2363) have observed that the green fluorescence of acetone vapour is replaced by a less bright blue fluorescence by the introduction of oxygen. The authors are of opinion that even in absence of oxygen the fluorescent radiations of acetone contain blue rays, which are masked by the more intense green fluorescence and that the oxidation, instead of producing a blue fluorescence, merely quenches the green and permits the blue to be more prominent. Fluorescence of acetone vapour on illumination has been found to be a comparatively

unimportant factor in the photolysis and photo-oxidation of acetone. Similar results in which the introduction of oxygen causes the decrease of light emission of acetone vapour have also been observed by Crone and Norrish (*Nature*, 1933, **132**, 241). These authors have claimed that they were the first to observe in the fluorescent spectra the phenomenon of predissociation, which has been generally observed in the absorption spectra only, but Turner (*Phys. Rev.*, 1932, **41**, 627) has also recorded the phenomenon of predissociation in the fluorescence spectra of iodine vapour. The decrease in the light emission of acetone vapour on illumination in presence of oxygen is in agreement with our view that increase in the chemical reactivity of acetone due to the presence of oxygen leads to the increase in the light absorption. Similar results are obtained with iodine vopour. It is known that predissociation of molecules can be induced or increased by collisions in some cases and atoms of iodine are generated in iodine vapour when illuminated by radiations of wave-lengths less than 5100Å if argon is present. The argon quenches the fluorescence of the higher vibrational states of the iodine molecules.

It is well known that the phenomenon of adsorption of a substance on a surface is more or less allied to chemical combination. Recently deBoer and Custers (*Z. physikal. Chem.*, 1933, **B**, **21**, 208) have shown that the light absorption of iodine adsorbed on a CaF_2 film is much greater than that of gaseous or dissolved iodine in water.

The views advanced in this paper are also supported by the observations of Fajans and Karagunis (*Z. physikal. Chem.*, 1929, **B**, **5**, 385) on the light absorption by silver iodide. The authors have shown that the light absorption by silver iodide containing adsorbed silver is appreciably greater than that of silver iodide, containing adsorbed iodine or silver iodide alone. Moreover, it is well known that the silver halides containing adsorbed silver are more photosensitive and hence more liable to be decomposed in light than the silver halides containing an excess of the halogen. Similar results have been obtained with other silver halides. The presence of silver sensitises the photo-decomposition of silver halides and weakens the binding forces between silver and the halogen atoms and causes increased light absorption.

The observations of Vogt and Kôenigsberger (*Z. Physik*, 1923, **13**, 292) on the influence of temperature on the continuous absorption of

bromine and iodine and of Gibson and Bayliss (*Phys. Rev.*, 1933, **44**, 188) with chlorine seem to show that increased temperature leads to a general broadening of absorption.

According to London's theory of chemical attraction, the production of an additive compound, not necessarily stable, formed by mixing two or more substances is essentially the first step requiring activation in a bimolecular exchange reaction. It appears that in general the formation of an additive compound with loosening of the binding forces of the molecules and consequent increased light absorption is the first stage of a chemical reaction.

We are expecting that in many cases we shall be in a position to calculate the energy of dissociation of molecules from measurements of increased light absorption by mixtures of reacting substances.

When the light absorptions of the reactions of $K_2C_2O_4+Cl_2$, $K_2C_2O_4+Br_2$ and $K_2C_2O_4+I_2$, are compared, it will be observed that the absorption due to $K_2C_2O_4+Cl_2$ is the maximum, then comes $K_2C_2O_4+Br_2$ and finally $K_2C_2O_4+I_2$. The heats of the reactions as calculated from the thermochemical measurements of Thomsen are as follows: $K_2C_2O_4+Cl_2$, 84 Cal; $K_2C_2O_4+Br_2$, 62 Cal; $K_2C_2O_4+I_2$, 32 Cal; but the energies of activation of the three reactions are in the reverse order, the iodine reaction has the largest and the chlorine the least energy of activation. Moreover, it is well known that the dissociation energies of the halogen molecules are as follows: Cl_2, 57 Cal; Br_2, 45 Cal; I_2, 35 Cal. It seems, therefore, that the dissociation energies of halogens are in the same order as their light absorption in presence of $K_2C_2O_4$. Moreover, it should be noted that the light absorption is generally more prominent in those reactions, which proceed at a greater velocity than in those, where the velocities are small. Thus in the reactions with halogens and potassium oxalate, the velocity is maximum with chlorine and minimum with iodine and the increased light absorption of the mixtures is in the same order.

Summary.

(A) It has been observed that the light absorption by a mixture of the reacting substances is greater than the absorptions by the ingredients with following reactions:

(1) Oxalic acid and chlorine, (2) potassium oxalate and bromine, (3) tartaric acid and bromine, (4) potassium oxalate and iodine,

(5) sodium formate and iodine, (6) acetone and iodine, (7) ferrous sulphate and iodine, (8) sodium nitrite and iodine, (9) sodium tartrate and iodine, (10) sodium lactate and iodine, (11) sodium malonate and iodine, (12) sodium malate and iodine, (13) sodium citrate and iodine, (14) hydroxylamine hydrochloride and iodine, (15) hydrazine sulphate and iodine, (16) hypophosphorous acid and iodine, (17) phosphorous acid and iodine, (18) quinine sulphate and chromic acid, (19) oxalic acid and chromic acid, (20) formic acid and chromic acid, (21) hypophosphorous acid and chromic acid, (22) phosphorous acid and chromic acid, (23) oxalic acid and potassium permanganate, (24) hydrochloric acid and potassium permanganate, (25) mercuric chloride and hypophosphorous acid, (26) mercuric chloride and phosphorous acid, (27) silver nitrate and sodium formate, (28) silver nitrate and ferrous ammonium sulphate, (29) hydrogen peroxide and sodium thiosulphate, (30) hydrogen peroxide and glucose, (31) hydrogen peroxide and potassium persulphate, (32) acetic acid and oxygen, (33) glycine and oxygen, (34) iodic acid and oxalic acid, (35) hydrolysis of cane sugar.

(B) The increased light absorption appears to be due to the activation of the molecules by the presence of the molecules of the other substances. The activation of the molecules is associated with the weakening of their binding forces and consequent increased light absorption.

(C) The observation of Weigert and Kellermann on increased light absorption by a mixtnre of chlorine and hydrogen and the increased light absorption observed by Ghosh and collaborators with mixture of Fehling's or Benedict's solutions and mixtures of reducing agents, and the observations of Fajans on increased light absorption by silver halides containing adsorbed silver, have been explained from the view point that the chemical reactivity of these various systems is associated with the weakening of the binding force and increased light absorption.

(D) The reactions with greater velocity appear to show greater light absorption than those with small velocities.

(E) It seems that the energies of dissociation of some molecules can be determined from measurements of increased light absorption by mixtures.

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FIG. 1.

Exposure—15″

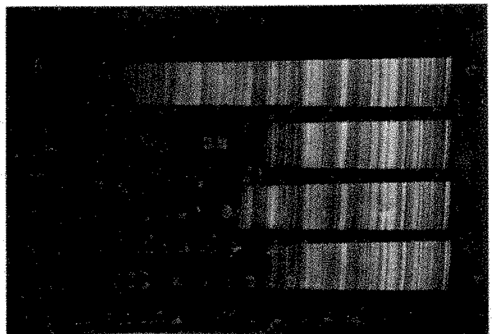


FIG. 2.

Exposure—7″

The velocity of the reaction of $K_2C_2O_4$ with halogens is in the order $Cl_2 > Br_2 > I_2$. The light absorption follows the same order.

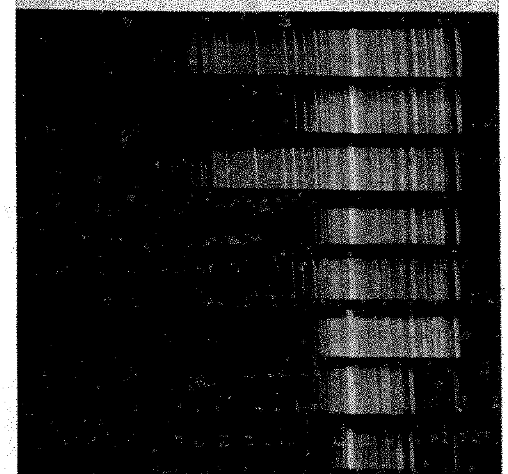
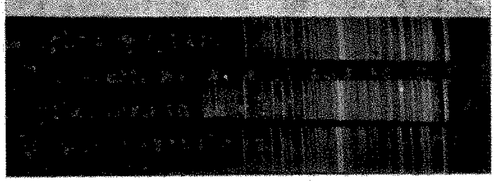


FIG. 3.

Exposure—15″

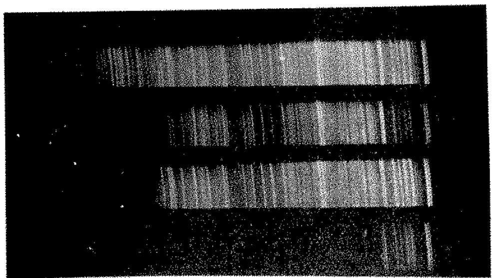


2017 2149 2294 2618 3274 5153Å

FIG. 4.

Exopsure—20″

The velocity of the reaction between Na-formate $+ I_2 > K_2C_2O_4 + I_2$. Light absorption is in the same order.



Arc

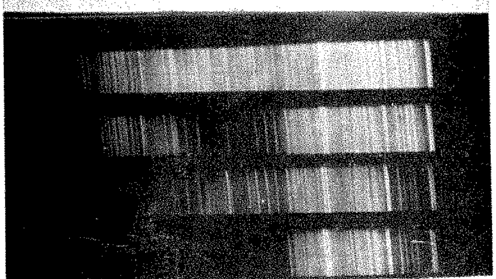
$N/700 - I_2$

$N/4$—Na-formate

$N/2$—Na-formate $+ N/350 - I_2$

FIG. 5.

Exposure—30″



Arc

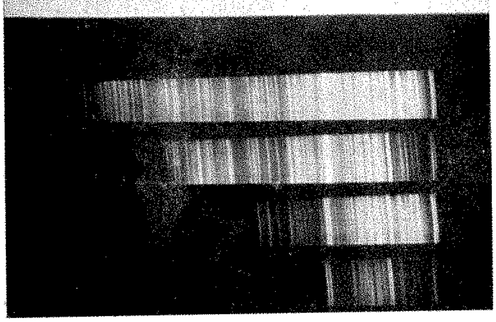
0·26% Acetone (HCl)

$N/700 - I_2$ (HCl)

0·5% Acetone $+ N/350 - I_2$ (HCl)

FIG. 6.

Exposure—7″



Arc

$N/1200 - I_2$

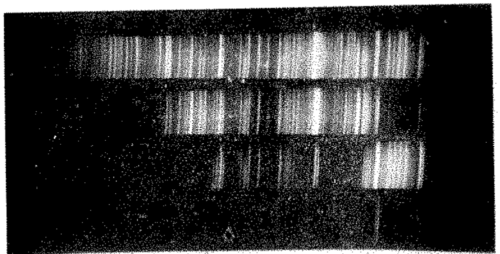
1% $FeSO_4$

$N/600 - I_2 + 2\% \; FeSO_4$

2079 2149 2294 2618 3274 5153 Å

FIG. 7.

Exposure—7″



Arc

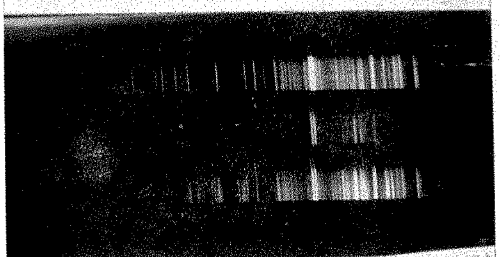
$N/700$—I_2

$N/16{\cdot}8$—$NaNO_2$

$N/350$—I_2 + $N/8{\cdot}4$ -Na NO_2

FIG. 8.

Exposure—7″



Arc

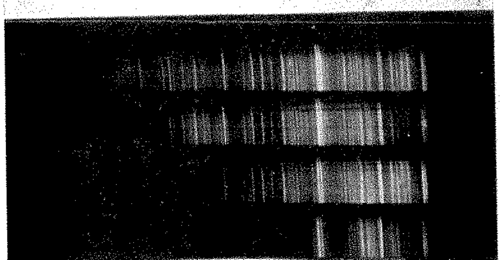
$N/500$—I_2

$N/2$—Na-tartrate

$N/250$—I_2 + Na-tartrate

FIG. 9.

Exposure—7″



Arc

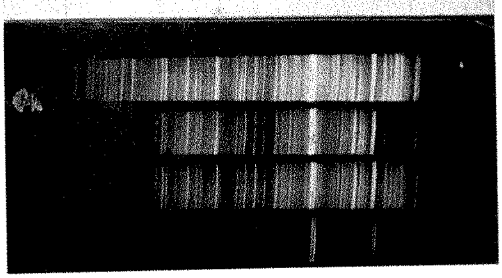
$N/700$—I_2

$N/2$—Na-lactate

$N/350$—I_2 + N-Na-lactate

FIG. 10.

Exposure—7″



Arc

$N/700$—I_2

$N/17{\cdot}6$—Na-malonate

$N/350$—I_2 + $N/8{\cdot}8$—Na-malate

2149 2294 2618 3274 5153Å

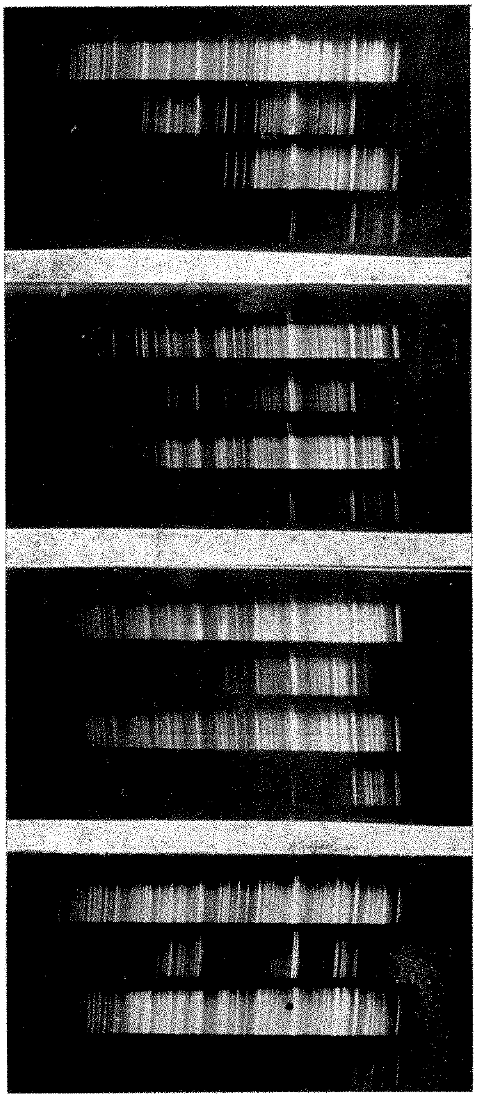


Fig. 11.
Exposure—7″

Arc
$N/700—I_2$
$N/27$—Na-malate
$N/350—I_2 + N/13·5$—Na-malate

Fig. 12.
Exposure—7″

Arc
$N/700—I_2$
$N/2$—Na-citrate
$N/350—I_2 + N$—Na-citrate

Fig. 13.
Exposure—7″

Arc
$N/700—I_2$
$N/10—NH_2OH·HCl$
$N/350—I_2 +$
$N/5—NH_2OH·HCl$

Fig. 14.
Exposure—7″

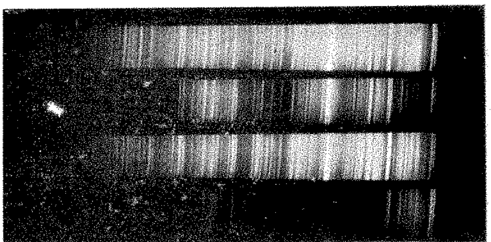
Arc
$N/700—I_2$ (H_2SO_4)
$N/8—NH_2·NH_2·H_2SO_4$ (H_2SO_4)
$N/350—I_2 + N/4—N_2H_4, H_2SO_4$ (H_2SO_4)

2149 2201 2618 3274 5153Å

FIG. 15.

Exposure—7″

Reaction of $H_2PO_2 + I_2 >$ $H_3PO_3 + I_2$ under identical conditions. Light absorption is greater in the former case than the latter.



rc

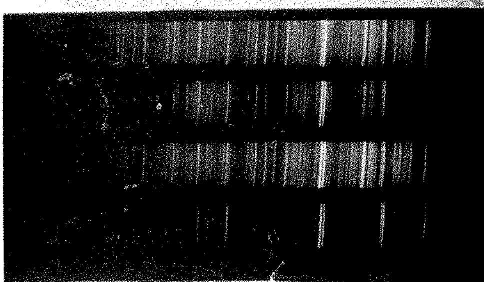
$N/700 - I_2$

$N/4{\cdot}3 - H_3PO_3$

$N/350 - I_2 +$ $N/2{\cdot}5 - H_3PO_2$

FIG. 16.

Exposure—7″



Arc

$N/700 - I_2$

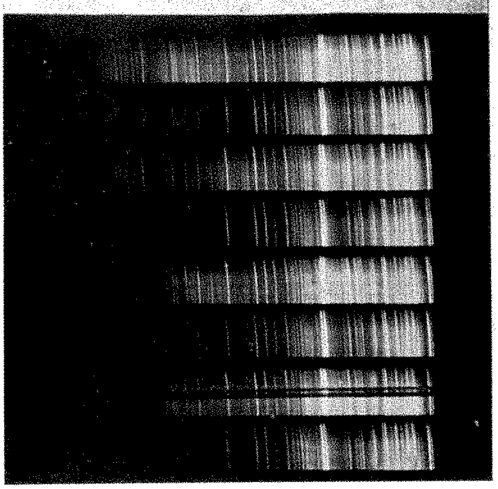
$10{\cdot}9N - H_3PO_3$

$N/350 - I_2 +$ $21{\cdot}8\,N - H_3PO_3$

FIG. 17.

Exposure—15″

Reaction of chromic acid + $C_2H_2O_4 >$ chromic acid + H_2CO_2. Light absorption is greater in the former.



Arc

$N/1656 - H_2Cr_2O_7$

0·04% – quinine sulphate

$N/828 - H_2Cr_2O_7 +$ 0·08% quin. sulph.

$N/11{\cdot}9 - CH_2O_2$

$N/828 - H_2Cr_2O_7 +$ $N/5{\cdot}95 - CH_2O_2$

$N/200 - C_2H_2O_4$

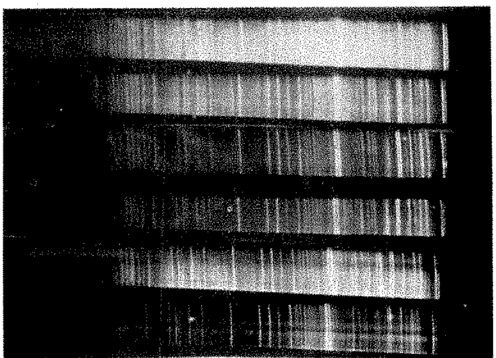
$N/828 - H_2Cr_2O_7 +$ $N/100 - C_2H_2O_4$

2149 2294 2168 3274 153Å

FIG. 18.

Exposure—15″

Reaction of chromic acid + H_3PO_2 > chromic acid + H_3PO_3. The former absorbs more light.



Arc

$N/119 - H_3PO_2$

$N/2232 - H_2Cr_2O_7$

$N/59{\cdot}5 - H_3PO_3 + N/1116 - H_2Cr_2O_7$

$N/14{\cdot}3 - H_3PO_2$

$N/7{\cdot}15 - H_3PO_2 + N/1116 - H_2Cr_2O_7$

FIG. 19.

Exposure—15″

Arc

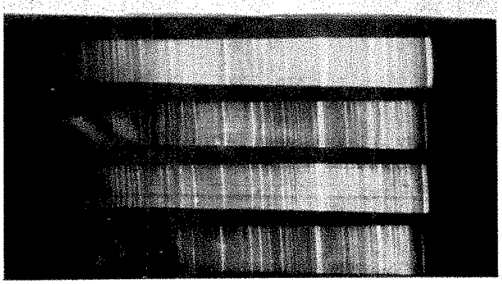
$N/200 - KMnO_4$

$N/40 - C_2H_2O_4$

$N/100 - KMnO_4 + N/20 - C_2H_2O_4$

FIG. 20.

Exposure—15″



Arc

$N/800 - KMnO_4$

$N/2 - HCl$

$N/400 - KMnO_4 + N - HCl$

2149 2294 2618 3274 5153Å

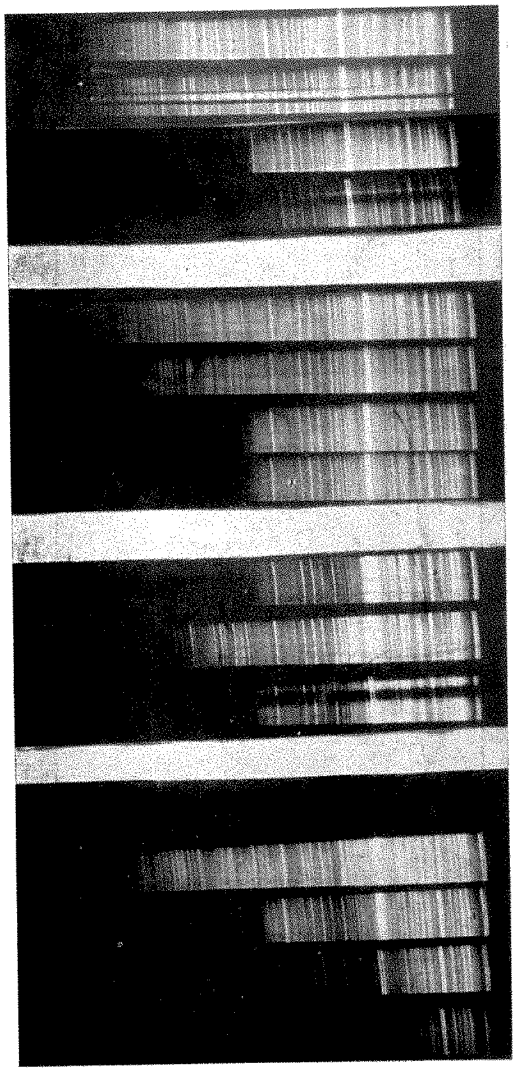


Fig. 21.

Exposure—7″

Arc

$N/14{\cdot}3 - H_3PO_2$

$N/18 - HgCl_2$

$N/7{\cdot}15 - H_3PO_2 +$
$N/9 - HgCl_2$

Fig. 22.

Exposure—7″

Arc

$N/119 - H_3PO_3$

$N/36 - HgCl_2$

$N/59{\cdot}5 - H_3PO_3 +$
$N/18 - HgCl_2$

Fig. 23.

Exposure—7″
Reaction of $AgNO_3$ + Fe-Am. sulphate appears faster than $AgNO_3 + NaH_2CO_2$-Former absorbs more light.

0·5% $AgNO_3$

0·5% $NaHCO_2$

1% $AgNO_3$ +
1% $NaHCO_2$

Fig. 24.

Exposure—7″

Arc

0·5% $AgNO_3$

1% Fe Am. Sulphate

1% $AgNO_3$ +
2% Fe Am. sulphate.

2149 2294 2618 3274 5153Å

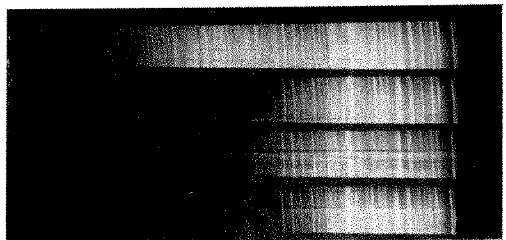


Fig. 25.
Exposure—15″

Arc

0·184% H_2O_2

N/982 – $Na_2S_2O_3$

0·368% H_2O_2 + N/491 $Na_2S_2O_3$

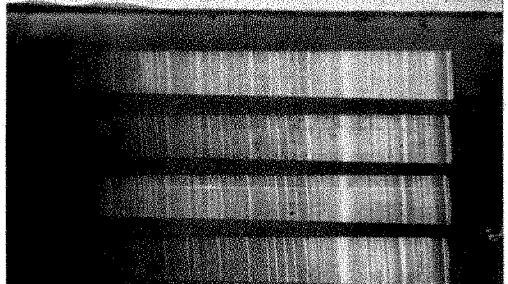


Fig. 26.
Exposure—15″

Arc

0·0184% H_2O_2

1·25% glucose

0·0368% H_2O_2 + 2·5% glucose

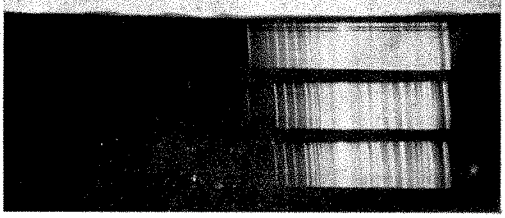


Fig. 27.
Exposure—15″

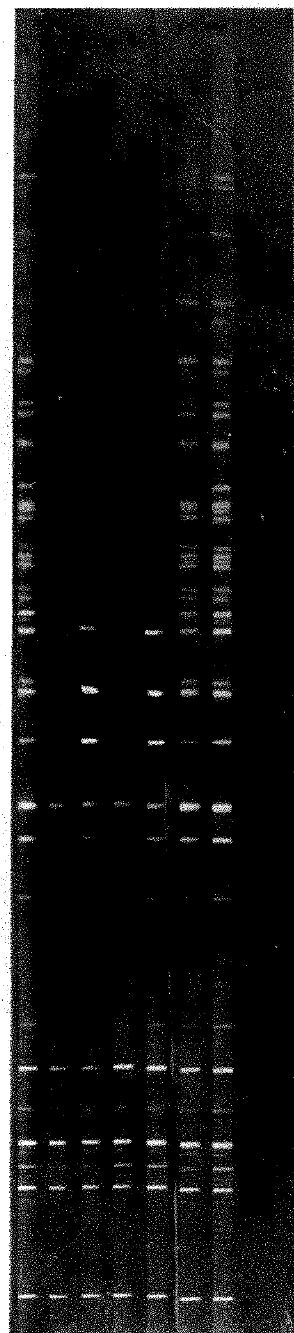
1% $K_2S_2O_8$

0·184% H_2O_2

0·368% H_2O_2 + 2% $K_2S_2O_8$

FIG. 28.

Exposure—30″



2122Å
2130
2135
2149
2178
2199
2215
2227
2246
2293
2319
2369
2392
2448

7 6 5 4 3 2 1

1. Arc.
2. Water saturated in oxygen.
3. $N/40$ Acetic acid
4. $N/40$-Acetic acid saturated with O_2.
5. $N/40$-Glycine.
6. $N/40$-Glycine saturated with O_2.
7. Distilled water.

2618 3274 5153Å

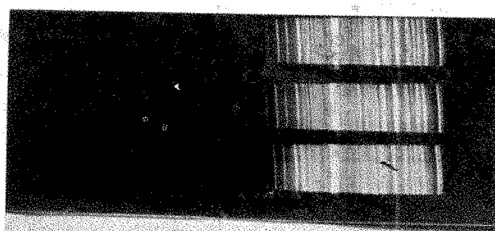


FIG. 29.

Exposure—15″

$N/20-HIO_3$

$N/10-H_2C_2O_4$

$N/10-HIO_3+N/5-H_2C_2O_4$

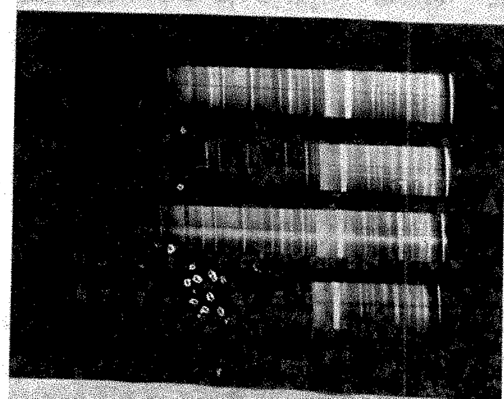


FIG. 30.

Exposure—15″

Arc

20% Cane sugar

$N/40-HCl$

40% Cane sugar + $N/20-HCl$

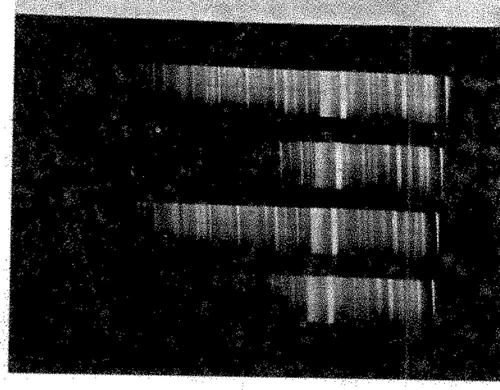


FIG. 31.

Exposure—15″

Arc

$N/40-C_2H_2O_4$

$N/80-HCl$

$N/20-C_2H_2O_4+N/40-HCl$

Composition of Prussian and Turnbull's Blue. Part II. Study of the Constituents of their Filtrates.

By Abani K. Bhattacharya.

In a previous communication (*Z. anorg. Chem.*, 1933, **213**, 240) it has been shown that Prussian and Turnbull's blue differ in their composition when freshly prepared by mixing the reacting constituents in equivalent proportions; but on ageing, the two compounds tend to be identical in composition and to assume a formula which is the mean of Prussian and Turnbull's blue, $Fe_4[Fe(CN)_6]_3$ and $Fe_3[Fe(CN)_6]_2$ respectively; or in other words, both the blues tend to approach the simplest formula $Fe_2(CN)_5$ wherein Fe : CN = 1 : 2·5.

It had also been urged that during the precipitation of Prussian blue, formation of some ferrous and ferricyanogen ion takes place as a result of mutual oxidation and reduction. Similarly during the precipitation of Turnbull's blue there would be some ferric and ferrocyanogen ions produced. In consequence of this, both Prussian and Turnbull's blue would tend towards a composition intermediate between ferrous ferricyanide and ferric ferricyanide.

The analysis of the filtrates of Prussian and Turnbull's blue was carried out to find whether mutual oxidation and reduction actually took place and the results are recorded in this paper.

The filtrates of the blues were prepared by mixing the solutions of the reacting substances in equivalent proportions. The mixture was made up to a litre in each case and the supernatant liquid was tested for the products of mutual oxidation and reduction as well as for the residual reactants.

When ferric chloride and potassium ferricyanide are mixed in equivalent proportions, no residual reactants could be detected with filtrate but when potassium ferrocyanide is added in excess, ferricyanide appears in the filtrate as shown by the liberation of iodine from potassium iodide. The filtrate does not give any test for ferrous sulphate, no matter in what proportions the reactants are added.

When ferrous sulphate and potassium ferricyanide are mixed in equivalent proportion, an appreciable amount of ferrous sulphate and a trace of ferric salt appear in the filtrate. If potassium ferricyanide is added in excess, the filtrate decolourises very dilute solution of potassium permanganate showing the formation of ferrocyanide. This has also been confirmed by mixing small quantities of ferric chloride to the solution of ferrous sulphate before addition of an equivalent quantity of ferricyanide.

TABLE I.

$M/2{\cdot}5$-$FeSO_4$ mixed with varying quantities of $M/2{\cdot}5$-$FeCl_3$ was added to the required volume of $M/2{\cdot}5$-$K_3Fe(CN)_6$ so as to give total precipitate of 0·125 g. Total volume kept constant at 50 c.c.

$M/2{\cdot}5$-$FeCl_3$ added (c.c.)	0·1	0·2	0·3	0·4	0·5
Action of NH_4CNS	Nil	Nil	Nil	Red	Deep red

It follows from the above experiments that with the removal of ferric chloride, there should be a corresponding excess of ferrous sulphate that remains unacted upon at the end of the reaction; and this is also shown by experiments recorded in Table II.

TABLE II.

Equivalent quantities of $FeSO_4$ and $K_3Fe(CN)_6$ were mixed in presence of varying quantities of $FeCl_3$ as to give 0·25 g. of the precipitate. Total volume kept at 100 c.c. The ferrous salt, unacted upon, was titrated with $KMnO_4$.

$M/2{\cdot}5$-$FeCl_3$ added.	$N/26{\cdot}84$-$KMnO_4$ required.	$FeSO_4$ unreactad.
0 c.c.	3·0 c.c.	0·1698 g.
0·2	3 5	0·1982
0·4	4·0	0·2266
0·6	5·0	0 2834
0·8	5·0	0·2834

The foregoing observations lend support to the view that some potassium ferrocyanide is undoubtedly formed in the above reaction;

the ferrocyanide reacts with the little ferric chloride which had been added to ferrous sulphate before it was mixed with potassium ferricyanide.

It was further observed that the filtrate of Turnbull's blue decolourised permanganate solution even after the ferrous sulphate had been removed as hydroxide by ammonia. Qualitative test for cyanide gave no indication of its presence. The reducing constituent was found to be an oxalate when tested for in the usual way after removal of the sulphate from the filtrate.

TABLE III

Analysis of reducing substances.

Equivalent quantities of $FeSO_4$ and $K_3Fe(CN)_6$ were mixed in the following concentrations to produce 2·5 g. of the precipitate. Volume was kept constant at 1 litre. The values obtained on immediate titration with $KMnO_4$ correspond to ferrous salt and oxalate where ferrous salt was not removed and to only oxalate where ferrous salt had been removed as hydroxide. The values recorded after 24 hours correspond to total reducing substances in either cases. Estimations for 50 c.c. are given.

Conc. of mixing $FeSO_4 : K_3Fe(CN)_6$.	Reducing substances in terms of $N/5.15KMnO_4$. $FeSO_4$ present		$FeSO_4$ removed	
	Immediate reduction.	Total reduction.	Immediate reduction.	Total reduction.
$M/5 : M/5$	0·91 c.c.	2·36 c.c.	0·25 c.c.	0·77 c.c.
$M/10 : M/10$	0·91	2·36	0·25	0·77
$M/25 : M/25$	0·89	2·36	0·28	0·79

TABLE IV

Quantities of $FeSO_4$ and $H_2C_2O_4$ calculated from the results given in Table III.

Conc. of mixing	$FeSO_4$.	$H_2C_2O_4$.	Undetected reducing agents in terms of $N/5{\cdot}15$-$KMnO_4$.
$M/5 : M/5$	0·3894 g./litre	0·04370 g./litre	1·45 c.c.
$M/10 : M/10$	0·3894	0·04370	1·45
$M/25 : M/25$	0·3600	0·04392	1·47

Prussian blues prepared in the same proportions as given in the foregoing tables "by mixing ferric chloride with potassium ferrocyanide' were kept in the dark and also exposed to sunlight, but neither oxalic acid nor ferric or ferrous salts could be detected in their filtrates.

Discussion.

It seems that the appearance of potassium ferricyanide on adding excess of potassium ferrocyanide and its absence from the filtrate when ferric chloride and potassium ferrocyanide are mixed in equivalent proportions cannot be completely explained by a purely chemical explanation as given by Woringer (*Chem. Z.*, 1912, **36**, 78). In all probability, the phenomenon of adsorption plays also an important part in removing the free potassium ferricyanide which is formed in accordance with the following reactions:

$$4\ FeCl_3 + 3\ K_4Fe(CN)_6 = \underset{\text{Prussian blue.}}{Fe_4[Fe\ (CN)_6]_3} + 12KCl$$

$$FeCl_3 + K_4Fe\ (CN)_6 = FeCl_2 + KCl + K_3Fe(CN)_6$$

$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 = \underset{\text{Turnbull's blue.}}{Fe_3[Fe\ (CN)_6]_2}$$

$$[\text{Prussian and Turnbull's blues}] + K_3Fe\ (CN)_6\ (\text{residual}) \xrightarrow{\text{adsorbed}} [\text{precipitated blue}]\ Fe\ (CN)'''_6 + 3K^{\circ}.$$

Adsorption of $K_4Fe\ (CN)_6$ by Prussian blue and $K_3Fe(CN)_6$ by Turnbull's blue has been studied and the results published (*Z. anorg. Chem.*, 1933, **213**, 240) will show that potassium ferrocyanide is appreciably adsorbed by Prussian blue, and the adsorption of potassium ferricyanide by Turnbull's blue, though much less than the corresponding values of $K_4Fe(CN)_6$ adsorbed by Prussian blue, was not negligible. In view of the adsorption effects shown by Prussian blue, the author is of opinion that the little potassium ferricyanide that is formed by mutual oxidation and reduction is partly used up in forming ferrous ferricyanide or Turnbull's blue, and the residue is adsorbed by the precipitates, whereas, when potassium ferrocyanide is added in excess, the ferrocyanogen ions are sufficiently adsorbed by the precipitate and hence potassium ferricyanide is set free in the solution. It is also to be noted in the foregoing scheme of reactions

that for each molecule of potassium ferricyanide formed, only two-thirds of it is used up by ferrous chloride leaving a residual quantity of ferricyanide which, if not adsorbed by the precipitate, should appear in the solution and this condition is favoured by mixing potassium ferrocyanide in excess.

When ferrous sulphate is mixed with potassium ferricyanide, the following changes are likely to take place. :

$$\text{I.}\quad 3\,FeSO_4+2\,K_3Fe(CN)_6 = \underset{\text{Turnbull's blue.}}{Fe_3\,[Fe\,(CN)_6]_2}+3K_2SO_4$$

$$\text{II.}\quad 4\,FeSO_4+4K_3Fe\,(CN)_6+2\,H_2SO_4 = 3\,K_4Fe(CN)_6+$$

$$2Fe_2(SO_4)_3+H_4Fe(CN)_6$$

$$\text{III.}\quad 2\,Fe_2(SO_4)_3+3\,K_4Fe\,(CN)_6 = \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3}+6K_2SO_4$$

$$\text{IV.}\quad H_4Fe\,(CN)_6+H_2SO_4= FeSO_4+6\,HCN$$

$$\text{V.}\quad \begin{cases} HCN+H_3Fe(CN)_6= H_4Fe\,(CN)_6+CN \\ \quad\text{or} \\ 2\,HCN+O = H_2O+(CN)_2 \end{cases}$$

$$\text{VI.}\quad (CN)_2+4\,H_2O = \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2\,NH_3$$

According to the above scheme, the existence of residual ferrous sulphate in the filtrate can be explained as in equation (IV). The formation of oxalic acid may also be explained on the assumption that part of the hydrocyanic acid is oxidised to cyanogen $(CN)_2$, which on hydrolysis forms oxalic acid. For the other reducing agents not yet identified, it seems probable that nitrogeneous organic reducing substances are formed with the intervention of hydrocyanic acid.

When dried precipitates of Prussian and Turnbull's blues are boiled, a small fraction assumes a colloidal character. It is quite stable and coagulation can only be effected by adding an electrolyte.

Estimation of moisture in air-dried preparations of Prussian and Turnbull's blues was carried out by taking weighed quantities of them in a crucible and heating in the air oven at 100° till the weight was found constant. The following table gives the total amount of moisture retained by prussian and turnbull's blues.

TABLE V.

Conc. of mixing.	Moisture in Prussian blue	Moisture in Turnbull's blue.
$M/5 : M/5$	16·72 %	18·16 %
$M/10 : M/10$	15·79	17·47
$M/25 : M/25$	16·16	19·30
Average	16·22	18·30

The samples of the blues dried in steam oven on exposure to the atmosphere regained the moisture lost in several days, the rate of increase in weight of turnbull's blue being a little slow.

Experiments on the study of colloidal Prussian and Turnbull's blues are in progress.

SUMMARY.

1. The formation of some quantity of potassium ferricyanide on adding ferric chloride to potassium ferrocyanide has been detected when potassium ferrocyanide is in excess.

2. On adding ferrous sulphate to potassium ferricyanide, some quantity of potassium ferrocyanide is formed. This has been indirectly shown by the removal of ferric chloride already added to the reacting ferrous sulphate from the field of reaction when the latter acts on potassium ferricyanide.

3. Presence of oxalic acid has also been detected in the filtrate and estimated.

4. Percentage of moisture retained by Prussian and Turnbull's blues has been estimated and the change produced on boiling the blues in water for a few hours has been observed.

In conclusion, I express my indebtedness to Prof. N. R. Dhar and Dr. S. Ghosh for their help and interest in the work.

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Dark Reaction between Sodium Formate and iodine.

By S. S. Doosaj and W. V. Bhagwat.

The reaction between sodium formate and iodine was studied by Dhar (*J. Chem. Soc.*, 1917, **111**, 707) and the order of the reaction with respect to sodium formate and iodine was found to be unity. We have studied this reaction at different temperatures and have also determined the effect on sodium acetate, potassium chloride, potassium bromide and potassium iodide on this reaction. Our results are recorded below:.

Order of the Reaction.

This was determined by Ostwald's isolation method, by varying the concentration of sodium formate which was always kept high. Thus if k_1 and k_2 be the velocity coefficients when the concentrations of sodium formate are c_1 and c_2, then the order n of the reaction with respect to sodium formate is given by

$$n = \frac{\log k_1/k_2}{\log c_1/c_2}.$$

TABLE I.

$KI = 44{\cdot}664$ g./litre. $I_2 = 6{\cdot}6934$ g./litre. $HCOONa = 122$ g./litre. 50 C.c. of each solution mixed together and 10 c.c. of mixture titrated each time.

Time.	Thiosulphate required.	$k_1 = \frac{1}{t}\log a/a\text{-}x$.
0 min.	11 c.c.	
17	6·2	0·0146
40·25	2·85	0·0145
54	1·8	0·0144
	mean	0·0145

The velocity coefficients for other concentrations of sodium formate are given in Table II.

TABLE II.

I_2 : KI (g./litre).	Na formate (g./litre)	$k = \frac{1}{t} \log a/a\text{-}x$.	$n = \frac{\log k_1/k_2}{\log c_1/c_2}$
6·6934 I_2 + 44·664 KI	(*i*) 122	(*a*) 0·0143	$\log\frac{a}{b}/\log\frac{i}{ii} = 1$
	(*ii*) 97·6	(*b*) 0·0116	$\log\frac{c}{b}/\log\frac{iii}{ii} = 1$
	(*iii*) 36·6	(*c*) 0·00436	$\log\frac{d}{c}/\log\frac{iv}{iii} = 1$
	(*iv*) 12·2	(*d*) 0·00147	$\log\frac{e}{d}/\log\frac{v}{iv} = 1$
	(*v*) 6·1	(*e*) 0·000729	...

Hence the reaction is directly proportional to the concentration of iodine and also to the concentration of sodium formate and hence the total order of the reaction is 2.

Effect of Sodium Acetate.

Sodium formate is easily oxidised by iodine at the ordinary temperature and the course of the reaction is represented by the equation,

$$HCOONa + I_2 = NaI + HI + CO_2$$

Dhar (*loc. cit.*) has used an excess of sodium acetate to regulate the reaction as the hydrogen ions, formed as a product of the change. greatly retard the reaction. We have studied the effect of sodium acetate on this reaction and observed that when concentration of sodium formate is sufficiently high, the reaction velocity is regular even without the addition of sodium acetate and the amount of sodium acetate has practically no effect on the velocity constant.

TABLE III.

$KI = 44{\cdot}664$ g./litre. $I_2 = 6{\cdot}6934$ g./litre. $HCOONa = 122$ g./litre.

50 C.c. of I_2 solution + 50 c.c. of HCOONa solution mixed and 10 c.c of the mixture titrated each time at 30°.

Sodium acetate = nil			Sodium acetate = 6·884 g./100 c. c. mixture.		
Time.	Thio.	k_1.	Time.	Thio.	k_1.
0 min.	11 c.c.	—	0	13	—
17	6·2	0·0146	22	6·5	0 0136
40·25	2·85	0·0145	35	4·05	0·0144
54	1·8	0·0144	55	2·06	0·0146
		mean 0·0145			mean 0·0145

Other results are summarised in Table IV.

TABLE IV.

Na-acetate in g./100 c.c. mixture.	k_1 at 16°.	k_1 at 21°.	k_1 at 26°.
0	0·001673	0·00364	0·00756
5	0·001670	0·00364	0·00753
10	0·001670	0·00364	0·00753
20	0·001674	0·00364	0·00753

It is thus clear that sodium acetate is not necessary to regulate the reaction when the concentration of sodium formate is high.

Effect of Potassium Iodide.

This reaction is retarded by the addition of potassium iodide due to the decrease in the amount of free iodine as KI_3 is formed according to the equation $KI + I_2 \rightleftharpoons KI_3$.

TABLE V.

KI=2·2831 g./100 c.c. mixture at 21°			KI=7·2231 g./100 c.c. of the mixture.	
Time.	Thio.	k_1.	Thio.	k_1.
0 min.	16·6 c.c.	—	16·75 c.c.	—
25	13·45	0·00365	15·7	0·00112
50	9·9	0·00365	14·7	0·00113
75	8·8	0·00361	13·7	0·00116
	mean	0·00364	mean	0·00114

Other results may be summariesd as follows:

TABLE VI.

KI. g./100 c.c. of mixture.	k_1 at 21°.	k_1 at 26°.
2·2831	0·00364	0·007406
7·2331	0·00114	0·002654
12·2331	0·0008261	0·00160
22·2331	0·000820	...

TABLE VII.

Temp.	Ratio of k_1.	Ratio of KI conc.	Ratio of KI conc./ratio of k_1.
21°	3·28	3·21	1·00
	4·4	5·3	1·20
	11·4	10·1	0·90
26°	2·85	3·2	1·14
	4·62	5·3	1·14

The relation between the amount of KI and the velocity coefficient is represented in Table VII.

These results show that the velocity coefficient does not fall directly as the concentration of potassium iodide but by a power which is less than the direct.

Effect of Potassium Bromide.

It is observed that the velocity coefficient is unaffected by the addition of potassium bromide.

TABLE VIII.

Temp. = 21°		Temp. = 26°	
KBr (g./100 c.c. of mixture).	k_1.	KBr (g./100 c.c. of mixture).	k_1.
0	0·00408	0	0·00778
5	0·00408	5	0·00773
10	0·00404	10	0·00774
20	0·00409	20	0·00775

Effect of Potassium Chloride.

We have varied the concentration of potassium chloride and observed that the velocity of the reaction increases with the concentration of potassium chloride. Ghosh and Purkayastha (*Z. physikal. Chem.*, 1930, **B.**, 7, 276, 285), has observed the same in case of the reactions between organo-hydroxy acids and bromine. Our results are given in Table IX.

TABLE IX.

Temp. 21°.

KCl = nil.			KCl = 8·987 g./100 c.c. mixture.		
Time.	Thio.	k_1.	Time.	Thio.	k_1.
0 min	15·8 c.c.	—	0	15·1 c.c.	—
25	12·4	0·00365	20	12·2	0·00481
40	10·9	0·00368	40	9·6	0·00491
60	9·25	0·00365	60	7·9	0·00470
	mean	0·00366		mean	0·00481

Other results are summarised in Table X.

TABLE X.

Temp.	KCl (g./100 c.c. of mixture).	Diff. in amount of KCl.	k_1.	Diff. in k_1.	$\frac{\text{Diff. of } k_1}{\text{Diff. of KCl}}$.
26°	0	—	0·00740	—	—
	5	5	0·00813	0·00073	0·000146
	10	10	0·00892	0·00152	0·000152
	20	20	0·01010	0·00270	0·000135

The results in the last column show that the increase in velocity coefficient is proportional to the concentration of KCl.

Temperature Coefficient of the Dark Reaction.

We have varied the amount of sodium formate and the velocity coefficient at different temperatures so obtained are summarised below.

TABLE XI.

Na-formate (g./litre)	100	80	50	30
k_1 at 16° ...	0·00161	0·00130	0·000788	0·000549
k_1 at 21° ..	0·00368	0·00290	0·00183	0·00116
k_1 at 26° ...	0·00753	0·00618	0·00393	0·00225

TABLE XII.

Na-formate (g./litre).	Temp. coeff. k_{21}/k_{16}.	Temp. coeff. k_{26}/k_{21}.	Temp. coeff. k_{26}/k_{16}.
100	$\frac{0·00366}{0·00166}=2·2$	$\frac{0·00753}{0·00366}=2·05$	$\frac{0·00753}{0·00166}=4·5$
80	$\frac{0·00290}{0·00130}=2·2$	$\frac{0·00618}{0·00290}=2·1$	$\frac{0·00618}{0·00130}=4·7$
50	$\frac{0·00183}{0·000788}=2·3$	$\frac{0·00393}{0·00183}=2·1$	$\frac{0·00398}{0·000788}=4·9$
30	$\frac{0·00116}{0·000549}=2·1$	$\frac{0·00225}{0·00116}=2·07$	$\frac{0·00225}{0·000549}=4·1$

These results clearly show that the value of temperature coefficient increases as the velocity constant falls. Thus the dark temperature coefficient or the acceleration of the dark reaction depends on the initial velocity. If this is smaller, the acceleration is larger or the temperature coefficient is greater than when initial velocity is great. This is quite obvious, because the acceleration depends on the number of active molecules increased, and always the same fraction of inactive molecules is activated according to Maxwell's rule. Hence, when the velocity is small the number of inactive molecules is great and hence the acceleration due to temperature or temperature coefficient is great.

TABLE XIII.

Reaction with aqueous iodine.

I_2=0·206 g./litre. HCOONa=4 g./litre. 50 c.c. of each solution mixed together and 10 c.c. of mixture titrated each time. Temp. =16°.

Time.	Thio.	k_1.
0 min.	20·6 c.c.	—
30	12·8	0·00689
60	8·6	0·00634
90	4·95	0·00680
	mean	0·00667

TABLE XIV.

Velocity constant with the concentration of formate at 16°.

Na-formate (g./litre).	k_1.	k_1 calc. on proportionality basis.
4·0	0·00667	0·00667
3·2	0·00536	0·00533
2·0	0·00328	0·00333
1·2	0·00212	0·00201

Thus the reaction is unimolecular with respect to both sodium formate and iodine.

Ghosh and Purkaystha (*loc, cit.*) have suggested from their experiments with bromine and organo-hydroxy acids that the order of the reaction with respect to halogen is bimollcular. Our results clearly have shown that at least in case of iodine, even in aqueous solution without the presence of KI, the order is unimolecular.

These observations therefore support the view of Bhagwat and Dhar (*Z. anorg. Chem.*, 1931, **191**, 393) that the order of the reaction with respect to iodine is unimolecular in such cases.

The comparison of the results clearly shows that the velocity constant has tremendously increased in case of aqueous iodine for the same concentration of sodium formate. It is about 3000 times greater than the velocity when 44·6684 g. of KI per litre are present.

Summary.

1. The dark reaction between sodium formate and iodine both in presence and absence of potassium iodide has been investigated and it is shown that order of the reaction with respect to iodine is always unity and never bimolecular as suggested by Ghosh and Purkaystha in case of bromine reaction.

2. The study of the effect of potassium chloride, potassium bromide, potassium iodide and potassium acetate shows that the reaction is accelerated by KCl and acceleration is proportional to the concentration of KCl. While KI retards the reaction KBr, has no effect on the reaction. It seems, therefore, that retarding effect of KI is due to the formation of KI_3 with I_2 thus diminishing the concentration of free iodine. It is found that when concentration of the sodium formate is high it is not necessary to add sodium acetate to get good velocity constants.

3. Measurements of temperature coefficient show that the value depends upon previous acceleration; greater the previous acceleration, smaller the temperature coefficient.

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Amylase from Sweet Potato (*Ipomoea Batatas*).

By K. Venkata Giri.

Among plant amylases, those from leaves and grains have been most studied, but only comparatively meagre information is available regarding the nature and behaviour of amylases from tubers.

Payen and Persoz (*Annalen*, 1834, **53**, 73 ; **56**, 337) were the first to observe the presence of amylase in germinating potato, but very little fresh information was added by later workers. Chrzaszez and Kostytschew, (*Woch. Barau.*, 1902, **25**, 105), Kostytschew, (*Ber. Bot. Ges.*, 1913, **31**, 125), Windisch and Jetter (*Z. Spiritusind*, 1907, **30**, 554), Heinzelmann, (*ibid.*, 1908, **31**, 12) until Doby (*Biochem. Z.*, 1914, **67**, 166) and Doby and Burger (*Fermentforse*, 1932, **13**, 201) made a systematic study of the various factors that influence the activity of potato amylase.

The observations of Doby (*loc. cit.*) as also the later ones of Haehn and Schweigart (*Biochem. Z.*, 1923, **143**, 516) led to the conclusion that potato amylase resembles animal amlyases in its behaviour towards salts, amino acids, hydrogen-ion concentration and temperature changes. McGuire and Falk (*J. Gen. Physiol.*, 1920, **2**, 215) have shown that the optimum reaction for potato amylase lies at p_H 6·7. Borchardt and Pringsheim (*Biochem. Z.*, 1931, **239**, 193) obtained evidence to show that potato amlyase occupies an intermediate position between the malt amylase which is particularly rich in β-amylase, and the taka-amylase which is pure α-amylase.

In view of the importance of the foregoing observations and the inadequacy of our knowledge regarding other tuber amylases, the present investigation on the amylase from sweet potato was undertaken.

Sweet potato is a common vegetable which is extensively cultivated in India. It is commonly used as food, cooked in curry or boiled, roasted or fried. Two forms are met with, one the red and the other the white tuber. Both the forms contain about 10 to 20% of sugar and about 16% of starch (*cf.* Watt, "The Commercial Products of India," 1908, p. 687).

The importance of the study of amylase present in sweet potato can be seen in the extensive application of the enzyme in industries like syrup manufacture, where it is employed to remove starch, which is responsible for the jellying and for the difficulty with which the syrup filters. In view of the possibilities of manufacturing syrup from sweet potato (Gore, Raese and Reed, *Chem. Age*, 1921, **29**, 151) a knowledge of the characteristics and the rôle played by the amylase present in the tuber is of great value in controlling the conditions for successful operation of the method.

Gore (*Ann. Food J.*, 1923, **18**, 519) has shown that maltose is formed on cooking sweet potato and this is attributed presumably to the presence of diastase in the tuber.

Hasselbring and Hawkins (*J. Agric. Res.*, 1915, **5**, 331, 543) have investigated the general course of carbohydrate transformation in sweet potatoes, during storage, and observed that in the stored sweet potato starch is first converted into reducing sugars, and finally cane sugar is synthesised from reducing sugars. Here again a study of the rôle played by amylase present in the tuber is of great importance in elucidating the physiological changes taking place in the tuber during storage and germination.

The present communication relates to the characteristics and mode of action of the sweet potato amylase, its function in the tuber and finally its comparison with amylases from other sources.

Experimemtal.

Preparation of the enzyme.—For the larger part of this work fresh tubers (red variety) were obtained from the market. An active preparation of the amylase can be obtained by pressing the juice from the tuber in a hydraulic press. The juice thus obtained is a light brown and opalescent liquid, and contains the amylase. The juice does not, however, keep well, so other methods of preparing the enzyme from dry material had to be adopted.

After mincing the tuber in a chopper, the ground tissue was spread on enamelled trays and kept for drying in bright sun. By frequent turning, the material can be dried in 5-6 hours. The material should not be allowed to ferment, as the activity of the enzyme is generally reduced by fermentation. The sun dried material was ground to a fine powder and passed through a 40 mesh sieve. The powder can be preserved well in bottles without any loss of

amylolytic activity. The enzyme can be easily extracted from this powdered meal with water or aqueous glycerol. The extract can be purified by dialysis in collodion bags.

The enzyme can be obtained in a concentrated form by precipitation with alcohol from aqueuous extracts of the meal. 200 G. of dry powdered meal were extracted with 800 c. c. of water for 12 hours in presence of toluene. It was then filtered and centrifuged. The amylase was precipitated from the aqueuous extract by adding four times the volume of 95 % alcohol, and after the settling of the precipitate the top layer was syphoned off and the rest centrifuged. The sediment thus obtained was treated with absolute alcohol and ether and finally dried in a desiccator over anhydrous calcium chloride. The resultant powder is light brown in colour.

Methods of procedure.—Soluble starch prepared according to Zulkowsky was used as substrate. The hydrogen-ion concentration. of the reaction mixture was adjusted by addition of Walpole's acetate buffer (p_H 3·0 – 6·5). For high ranges of p_H, Sörensen's phosphate buffer was used. The enzyme solution was prepared by weighing a known amount of the enzyme powder, which was made into a paste with water and diluted to 100 c.c. It was prepared afresh for each experiment. The reactions were carried out at constant temperature in an electrically controlled thermostat.

The digestions were carried out in Erlenmeyer flasks with 100 c. c. lots of mixtures containing 1·5 g. of starch, buffer solution and enzyme. 10 C. c. samples were removed at intervals of 5, 10, 15, 20 and 30 minutes, and the reducing power determined by the method of Willstätter and Schudel (*Ber.*, 1918, **51**, 780). The degree of hydrolysis is expressed by the reducing power of the mixture. This is measured by the amount of maltose formed in the total volume (100 c. c) of the reaction mixture in a given time and the velocity constants for a unimolecular reaction were calculated according to Euler and Svanberg (*Z. physiol. Chem.*, 1920-21, **112**, 191), by applying the formula

$$k = \frac{1}{t} \log \frac{a}{a-x}$$

where t is the reaction time in minutes, a, the original concentration, x, the concentration of substrate decomposed and $a-x$, the concentration of the substrate present after t minutes. It was found that the unimolecular course of the reaction persists until 40—50 %

of the amount of maltose, formed on complete hydrolysis of the substrate, is present; on further hydrolysis, the rate of the reaction diminishes. The activity is given in terms of velocity constant k, and the activity unit (Sf) in terms of Euler's units.

Dialysis.—100 G. of powdered sweet potato meal was treated with 400 c. c. of distilled water in presence of toluene for about 16 hours at the laboratory temperature (28 – 30°). It was then filtered, centrifuged, and dialysed in collodion tubes against distilled water containing toluene which was renewed twice every day. Each collodion tube contained 20 c. c. of the enzyme extract. At definite intervals of time one tube was taken out, centrifuged, and finally diluted to 100 c. c. The activity of this diluted enzyme solution was then determined.

The values thus obtained were compared with those for specimens of the original enzyme extract which had been left undialysed. It was found, however, that the activity of the undialysed enzyme remained practically unaltered during the experimental period.

For each trial, the reaction mixture contained 75 c.c. of 2 % soluble starch, 20 c.c. of acetate buffer adjusted to p_H 6·0 and 5 c.c. of enzyme solution. The temperature was 30° ± 0·1°. The results have been given in Table I.

TABLE I.

Dialysis.

Dialysed for.	Dry wt. enzyme soln. (g./5 c.c.).	Activity $k \times 10^4$.	Activity unit Sf (30°).
0 hr.	0·042	88·1	0·236
16	0·0050	68·3	1·586
40	0·0035	41·8	1·34
80	0·0031	29·6	1·11
120	0·0025	14·3	0·634

The results show that the activity per unit weight of dry substance of the enzyme (Sf) increases after 16 to 40 hours of dialysis to nearly seven times. Dialysis can, therefore, be very effectively used as one of the methods for the purification of the enzyme.

These observations correspond to those of Euler and Svanberg (*Z. physiol. Chem.*, 1921, **112**, 193) and Holmberg, (*ibid.*, 1924, **134**,

68) who used dialysis for the purification of malt and liver amlyases respectively, and obtained products of greatly increased activity.

Influence of hydrogen ion concentration on the activity of the amylase.—Flasks containing 75 c. c. of 2 % soluble starch, 20 c. c. of buffer of varying hydrogen ion concentrations were kept in a thermostat at 35° ± 0·1°. When the reaction mixture had attained the temperature of the thermostat, 5 c. c. of the enzyme solution (0·1 %) were added, and the activity measured. The results are given in Table II.

TABLE II.

Starch conc. = 1·5%. Enzyme conc. = 0·0005%.

p_H ...	8·0	7·1	6·5	6·2	6·0	5·5	5·3	4·8	4·6	4·2	3·0
Activity ... $k \times 10^4$	25·8	53·4	82·1	90·3	114	114	96·9	91·4	76·7	52	25·7

It may be seen from the results that sweet potato amylase acts best in the region of p_H 5·5 – 6·0.

Influence of temperature on the activity of the amylase.—The reaction mixture consisting of 75 c.c. of 2 % soluble starch, 29 c. c. of buffer of p 6·0 and 5 c. c. of the enzyme solution (0·1 %) was maintained at temperatures of 20°, 30°, 35°, 40°, 50°, 55°, 60° and 70° in a thermostat and the activities measured. The results are presented in Table III.

TABLE III.

Starch conc. = 1·5%. Enzyme conc. = 0·005%. p_H = 6·0.

Temp. ...	20	30	35	40	45	50	55	60	70
Activity $k \times 10^4$ ...	39·4	79·7	99·5	117	134	150	151	125	24·9

The results show that the temperature optimum for sweet potato amylase lies in the region of 50°—55°. Comparing this with the optimum for other amylases it may be noted that it is 45° for salivary amylase (Oppenheimer, "Die Fermente und ihre wirkungen," Leipzig, 1903; Konig, *Biochem. Z.*, 1908, **10**, 211), 35° for pancreatic amylase (Vermon, *J. Physiol.*, 1901-02, **27**, 174), 40° for potato amylase (*Biochem. Z.*, 1914, **67**, 166) and between 50 and 56° for amylases of germinated grains (Effront, *Compt. rend. Soc. Biol.*,

1922, 86, 274; Patwardhan, *J. Ind. Inst. Sci.*, 1929, **12A**, 185; Karmarkar and Patwardhan, *ibid.*, 1930, **13A**, 169). It may be inferred, therefore, that potato amylase resembles animal amylases with regard to its temperature optimum, while the sweet potato amylase corresponds to cereal amylases.

Effect of temperature on the stability of sweet potato amylase.—In a previous communication on the heat inactivation of pancreatic amylase (Giri, *J. Ind. Inst. Sci.*, 1932, **15A**, 117) it was stated that the process of heat inactivation follows a monomolecular course. The rate of inactivation of pancreatic amylase is minimum at a p_H 6·5 to 7·0 in the neighbourhood of the optimum reaction for the enzyme. Since the inactivation of enzymes by heat has a large temperature coefficient, it is possible that inactivation can take place at ordinary laboratory temperatures at slower rates. Thus, it was observed (Giri and Subrahmanyan, *ibid.*, 1932, **15A**, 107) that vegetable amylases in aqueous solution lose their activity on ageing, and that they are most stable when maintained at their optimum p_H.

The following experiments were carried out in order to investigate the possibility of such inactivation (*vide*, Tables IV*a* and IV*b*).

(*a*) *Effect of temperature.*—10 C.c. of buffer mixtures (p_H 6·0) were kept in a thermostat at 50°, and when the temperature equilibrium was attained, 10 c.c. of 0·2% solution of the enzyme were added to each tube. At definite intervals of time 5 c.c. of the enzyme solution were pipetted out and the activity estimated at 30° and p_H 6·0. In a similar manner the inactivation of 0·1% amylase solution was carried at 60° and 65°. At higher temperatures the enzyme is very rapidly inactivated, so that the course of the reaction is difficult to follow. Simultaneously the activity of the enzyme solution of the same concentration which was kept at the room temperature (28°) was also determined. The experimental results are given in Table IV*a*.

From these experiments the value for the inactivation coefficient k_i is calculated from the equation

$$k_i = \frac{1}{t} \log \frac{k_a}{k_t}$$

where k_a is the reaction constant of the enzyme which is not destroyed, and k_t is the reaction constant of the same enzyme which has been weakened in activity as the result of heating for t minutes.

TABLE IV *a*.

Temp.	Time of inactivation.	Activity at 30° of the amylase not destroyed by inactivation $k \times 10^4$.	$k_i = \frac{1}{t} \log \frac{k_a}{k_t}$	k_i mean
50°	30 min.	68·9		
	60	68·9		
60°	10	62·8	0·00396	
	30	52·6	0·00388	·0036[illegible]
	60	43·9	0·00325	
65°	10	24·9	0·0220	
	30	14·3	0·0227	·0216
	60	4·7	0·0200	
Control	...	68·8		

The results indicate that the process of heat inactivation of sweet potato amylase follows a monomolecular course. The enzyme is able to withstand increased temperature up to 50°. At 60° the loss in activity is under 50%, but at 65° it is about 80 % of the initial activity.

The destructive temperature of enzymes has been defined by Euler ("Chemie der Enzyme," 2nd Ed., 1922, p. 314) as that at which the activity of the enzyme is reduced 50% in 1 hour at the optimum p_H. The destructive temperature of sweet potato amylase lies therefore between 60° and 65°. Malt amylase is destroyed in one hour at 60° and its destructive temperature lies at 54°-56° (Ernström, *Z. physiol. Chem.*, 1922, **119**, 190). Other plant amylases are more sensitive to temperature. Thus *phaseolus* amylase has its destructive temperature at 45° (Sjoberg, *Biochem. Z.*, 1923, **142**, 274) and Doby (*loc. cit.*) found the destructive temperature of potato amylase to lie at 45°. Animal amylases are inactivated even at ordinary laboratory temperatures (Giri, *loc. cit.*).

Sweet potato amylase differs therefore from animal amylases and potato amylase but it resembles cereal amylases in its heat stability. The amylase can, in fact, withstand higher temperatures that malt amylase.

(*b*) *The effect of hydrogen ion concentration on the inactivation of the amylase.*—Acetate buffer mixtures (10 c.c.) of different hydrogen-ion concentrations were prepared and placed in a thermostat at 60°. When the temperature equilibrium were attained, 10 c.c. of 0·2% solution of the amylase was added into each test tube. One hour after the addition of the amylase, 5 c.c. samples were taken out and transferred to the reaction mixture containing 75 c.c. of 2% soluble strach and 20 c.c. of buffer of p_H · 6·0. The activities were determined at 30° and are given in Table IV*b*.

TABLE IV *b*.

p_H ...	6·5	6·0	5·4	4·6
Activity of the amylase after heating at 60° for 60′ ($k \times 10^4$) ...	20·5	38·9	39·4	4·7
Activity of the amylase without heating ...	...	...	...	79·0

The above experiments show that the stability of sweet potato amylase is greatest in the region of p_H, 5·4 and 6·0 which is also the optimum range of p_H for activity. Thus the optima for activity and stability are found to be at the same range of p_H. A similar observation was made on the ageing of amylases in aqueous solutions (Giri and Subrahmanyan, *loc. cit.*). Working on the heat inactivation of pancreatic amylase, Giri (*loc. cit.*) found that the rate of inactivation is minimum at p 6·5 to 7·0, in the neighbourhood of the optimum reaction for the enzyme. Comparing these with the observations of other workers, it may be noted that Lüers and Lorinzer (*Biochem. Z.*, 1932, **133**, 487) found that the activity optimum and stability optimum for malt amylase was in the same range of hydrogen-ion concentration. Contrary to the observations of foregoing investigators Ernström (*Z. physiol. Chem.*, 1922, **119**, 190) found the stability optimum at a higher p_H than the activity-optimum. In the case of ptyalin, Ernström found the stability optimum at p_H 6·0, *i. e.*, to the acid side of the optimum p_H for activity. This divergence can be easily explained in the

light of investigations of Michaelis and his co-workers (*Biochem. Z.*, 1911, 35, 386; 1914, 59, 77) who have shown that the activity-p_H curves for ptyalin vary according to the presence and nature of the neutral salts employed, and that these changes have been explained by the assumption of the formation of different amylase electrolyte complexes having different dissociation constants. The experiments of Ernström on the determination of stability optimum p_H and activity optimum p_H were not carried out at the same salt concentration, because sodium chloride was not added in the inactivation experiment, though the optimum p_H was determined in presence of the salt. Furthermore Myrback (*Z. physiol. Chem.*, 1926, 159, 1) has shown that the activity optimum of ptyalin lies at p_H 6·0 for NaCl-free ptyalin, and the stability optimum also lies at p_H 6·0 according to Ernström. So, it can be definitely said that the stability optimum and activity optimum lie at the same range of p_H for ptyalin, pancreatic amylase, malt amylase and sweet potato amylase.

Distribution of amylase in sweet potato.—The tuber was divided into the following portions.—(*a*) the outermost portion (representing a layer of about 1 cm. thickness from the surface); (*b*) the middle portion (representing the next immediate layer of about 1 cm. thickness); and (*c*) the innermost portion (representing the remaining part of the tuber, the core).

These different parts were chopped, dried in the sun and powdered. The enzyme was extracted from 5 g. of the powdered meal with 20 c.c. of water for 12 hours, filtered and centrifuged. The activities of these extracts (diluted 10 times) were then determined. The results are presented in Table V.

TABLE V.

75 C.c. of 2% soluble starch; 20 c.c. of buffer of p_H 6·0, 5 c.c. of the enzyme solution. (Total conc. of starch =1·5% and the total volume=100 c.c.).

	Dry in g./5 c.c. of the enzyme solution.	Activity $k \times 10^4$.
(*a*) Activity of the amylase in the outermost portion	0·0249	18·7
(*b*) Activity of the amylase in the middle portion	0·0285	46·1
(*c*) Activity of the amylase in the innermost portion	0·0289	62·4

The same experiment was repeated with the juice expressed from different portions of the same tuber. The results thus obtained were similar to those of the previous experiment. The results thus show that amylolytic activity increases as we pass from the skin to the interior and that the innermost portion has more than thrice the activity of the outermost portion.

The nature of sweet potato amylase.—According to Ohlsson and his co-workers (*Compt. rend. Soc. Biol.*, 1922, **87**, 1183; and *Compt. rend. Trav. Lab. Carlsberb.*, 1926, No. 7, 16 ; Nordh and Ohlsson, *Z. physiol. Chem.*, 1931-32, **204**. 89 ; Ohlsson and Uddenberg, *ibid.*, 1933, **221**, 165 ; Ohlsson and Edfeldt, *ibid.*, 1933, **221**, 174) malt amylases of cereals consist of an α-or dextrinogen-amylase and of a β- or saccharogen-amylase, these being differentiated by studies of mutarotation as well as the relative hydrolysis as determined by changes in the iodine coloration and the reducing action. Nordh and Ohlsson (*loc. cit.*) and Myrback and Myrback (*Woch. Brau.*, 1932, **49**, 246) have shown that ungerminated barley contains mostly only β-amylase whilst after germination considerable amounts of α-amylase is formed. Contrary to Nordh and Ohlsson's view, Waldschmidt Leitz, Reichel and Purr (*Naturwiss.*, 1932, **20**, 254) have come to the conclusion that ungerminated barley contains both α-and β-amylases, but that the amylase is present in inactive form and requires amylokinase for activation. This kinase is developed during germination. Borchardt and Pringsheim (*loc. cit.*) working on the amylase, prepared from the press juice of the ground potato which was deproteinized with colloidal ferric hydroxide, have shown that the potato amylase apparently occupies an intermediate position between the malt amylase particularly rich in β-amylase and the taka amylase which is pure α-amylase, as it contains less β- than α-amylase. Willstätter and Rohdewald (*Z. physiol. Chem.*, 1933, **221**, 13) have shown that the amylases of leucocytes are dextrinogenic in character, thereby resembling pancreatic amylase and differing from malt amylase. The foregoing observations bring out a distinct difference between animal and vegetable amylases, the former belonging to the class of α-amylases and the latter to that of β-amylases. According to Pringsheim, however, potato amylase falls midway between the two main classes.

The following experiments were, therefore, conducted with a view to throwing light on the nature of sweet potato amylase and to compare it with that of barley malt amylase. Amylase from barley

malt was prepared by extracting powdered malt (200 g.) with 800 c. c. of water for 24 hours in presence of toluene and finally filtered and centrifuged. To 400 c. c. of the filtrate 1600, c. c. of 95 % alcohol was slowly added with stirring and the precipitate allowed to settle during 6-8 hours when the alcohol was syphoned off, the rest of the liquid then centrifuged, and the sediment thus obtained washed and dehydrated with absolute alcohol and ether and finally dried in a desiccator over anhydrous calcium chloride.

Solutions (0·1 %) of the two amylases were prepared and the activities of the saccharogenic (S), and dextrinogenic components measured.

The activity of the saccharogen amylase (S) was determined as follows. 25 c. c. of 2% soluble starch was placed in a flask together with 10 c. c. of buffer solution ($1/5M$-acetic acid – acetate mixture). The flask was placed in a thermostat at 38°. When the solution had attained the temperature of the water, 5 c. c. of the enzyme solution were added. After 30 minutes, 10 c. c. were removed and the reducing value determined and expressed as mg. of maltose. The hydrogen-ion concentration of the reaction mixture was adjusted to p_H 4·6 for barley malt amylase, and p_H 6·0 for sweet potato amylase.

The activity of the dextrinogen amylase (X and Y) was determined according to Ohlsson (*loc. cit.*). The results are presented in Table VI.

TABLE VI.

	Activity of saccharogen amylase. (S)	Activity of dextrinogen amylase. (X)	(Y)
Sweet potato amylase	59	0	12
Barley malt amylase	68	24	190

The above figures show that sweet potato amylase is mainly a saccharogen amlyase or β-amylase. Thus it differs from potato amylase and resembles barley amylase.

SUMMARY.

1. An active diastatic enzyme is present in sweet potato.

2. The enzyme can be prepared from the water extract of the dried meal followed by precipitation with alcohol. The preparation can

be further purified by dialysis as the result of which the activity is increased nearly seven times.

3. The optimum hydrogen ion concentration for the enzyme lies between p_H, 5·5 – 6·0.

4. The optimum temperature lies between 50° and 55°.

5. The process of heat inactivation of the amylase is found to follow a unimolecular course. The enzyme is most stable in the region of p_H 5·4 and 6·0, which is also the optimum range of p for activity.

6. The inner portion of the tuber possesses greater amylolytic activity than the layers near the surface.

7. The amylase is mainly a saccharogen amylase or β-amylase.

8. It resembles cereal amylases and differs from potato amylase as also similar enzymes of animal origin in all its characteristics.

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Halogenation. Part IX. Bromination of Pseudocumene.

By Phuldeo Sahay Varma and Dhirendra Nath Sen-Gupta.

By the action of bromine on pseudocumene in the cold nuclear substituted bromo derivatives and in sunlight in the cold a light oil and on heating to 160° pseudocumene dibromide and pseudocumene tribromide have been obtained (Beilstein, *Annalen*, 1866, **137**, 323; Fittig, *Annalen*, 1869, **151**, 267; Schram, *Ber.*, 1886, **9**, 217; Jacobsen, *Ber.*, 1888, **21**, 2822; Hjelt and Gadd, *Ber.*, 1886, **19**, 868).

We have obtained in sunlight either pseudocumene monobromide alone or a mixture of monobromide, dibromide and tribromide of pseudocumene depending on the conditions of the experiment. By brominating 5-bromopseudocumene in sunlight, only nuclear substituted derivatives of pseudocumene have been obtained. At the boiling temperature of pseudocumene in the diffused day light, only monobromide is obtained even when there is a considerable excess of bromine present. Comparatively good yields of the nuclear substituted bromo derivatives of pseudocumene are obtained, if bromination is carried on in presence of strong or fuming sulphuric acid or strong or fuming nitric acid or a mixture of nitrosulphonic and fuming nitric acids.

Experimental.

A mixture of pseudocumene (10 c.c.) and bromine (4·5 c.c.) was exposed to sunlight for about 3 hours. The reaction product was then heated further for 2 hours on a water-bath under reflux. The product was first washed thrice with 1% solution of sodium carbonate, then with water, dried over anhydrous calcium chloride and distilled at 152-56°/30 mm, yield 5·1 g. It is an oily lachrymatory substance. It darkens in colour on standing and becomes almost black after a few days. It decomposes on boiling at the ordinary pressure. (Found: Br, 41·2. $C_6H_3(Me_2CH_2Br$ requires Br, 40·2 per cent).

If exposure to sunlight was followed by heating on a water-bath, only monobromide was obtained whereas if it was followed by heating on a paraffin-bath to about the boiling point of pseudocumene, a mixture of mono-, di-, and tribromide was obtained, their relative proportions increasing by using bromine (3 to 6 c.c.).

Working in the same way with 5-bromopseudocumene in sunlight, followed by heating for about 3 hours on a water or a paraffin-bath only di- and trinuclear substituted bromo derivatives in fairly good yields were obtained.

If strong or fuming sulphuric acid or strong or fuming nitric acid or a mixture of nitrosulphonic and fuming nitric acid was added little at a time to a mixture of pseudocumene and bromine and the products formed examined after 3-4 hours, much better yield of the nuclear substituted bromo derivatives was obtained. The best yield (3-bromopseudocumene, 4·3 g ; 5-bromopseudocumene, 2·8 g.; 5 : 6-dibromopseudocumene, 1·2 g; and 3 : 5 : 6-tribromopseudocumene 2·2 g., from 10 c.c. of pseudocumene) was, however, obtained when bromination was carried on in presence of a mixture of nitrosulphonic and fuming nitric acids (10 c.c.)

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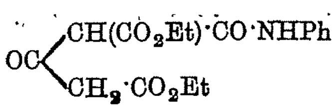
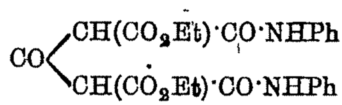
Extension of Michael's Reaction. Part IV.

By Tejendra Nath Ghosh and Praphulla Chandra Guha.

In previous parts of this series (Ghosh and Guha, *J. Indian Chem. Soc.*, 1930, **7**, 263) the action of mustard oils and *iso*cyanates has been studied upon various types of compounds containing one active methylene group. It seemed desirable to extend this type of condensation with compounds containing more than one active methylene group. Acetone dicarboxylic ester, in which there are two active methylene groups, was expected to yield compounds of the type I and II respectively with one or two molecules of mustard oils or *iso*cyanates.

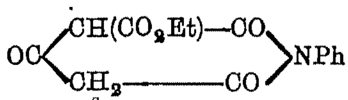


(I)



(II)

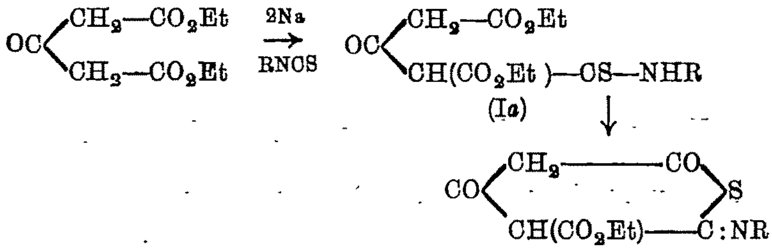
An unsuccessful attempt to effect ring-closure of thiocarbethoxy-acetoacetyl carbamic ester with the aid of sodium ethoxide for pyridine ring synthesis has been recorded by Ghosh and Guha (*J. Ind. Inst. Sci.*, 1933, **16A**, 103). The second object in undertaking the present investigation was to see whether arylcarbamylacetone dicarboxylic ester (type I) in presence of suitable ring-closing agents could be converted into a pyridine compound (III).



(III)

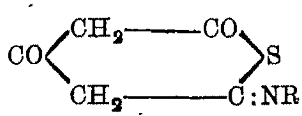
Ethylacetone dicarboxylate in presence of sodium (1 or 2 atoms) reacts with thiocarbimides (1 or 2 mols.) to give instead of the expec-

ted thio analogues of compounds (I), (II) or (III), a thiopyran compound (IV) according to the following scheme:



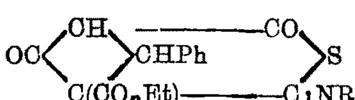
(IV)

The compound (I*a*), which is evidently formed as the first product in this reaction, possesses such a great tendency towards ring formation that its isolation was not possible. That the ring-closed compound possesses the formula (IV) and is not the pyridine derivative of type (III) is proved by the facts that (*a*) it is not endowed with any mercaptanic properties, (*b*) it cannot be desulphurised by mercuric oxide treatment proving thereby the presence of the sulphur atom as a member of the ring (*cf*. Busch and Wolpert, *Ber.*, 1901, **34**, 804; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502), (*c*) it gives on hydrolysis the compound (V).

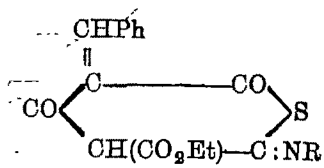


(V)

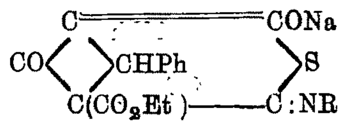
The compound (IV) reacts with benzaldehyde to yield a compound which can be represented by either of the two following formulæ (VI or VI*a*). In view of the fact that the original compound (IV) gives a disodium derivative whereas the benzaldehyde compound does not form any sodium salt, the formula (VI*a*) is rejected in preference to the bridged formula (VI), enolisation of (VI) into (VI*b*) and (VI*c*) being against Bredt's law (*Annalen*, 1924, **437**, 1).



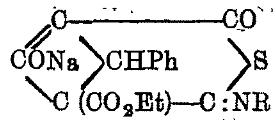
(VI)



(VIa)



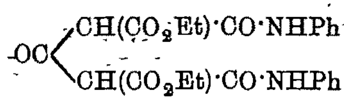
(VIb)



(VIc)

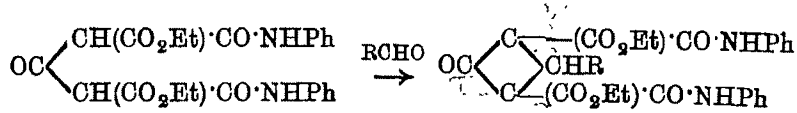
This reaction affords a new and convenient method for the synthesis of thiopyran rings.

Ethylacetone dicarboxylate reacts with phenyl *iso*cyanate to give the expected diphenylcarbamyl derivative (VII) which shows no tendency towards ring formation, this difference is evidently due to the thiocarbamyl groupings possessing greater capacity for ring formation.

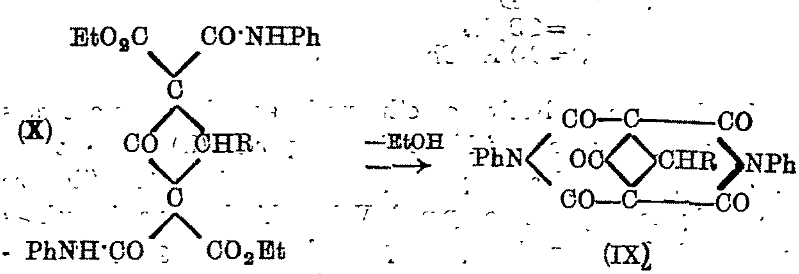


(VII)

The compound (VII) containing as it does two active hydrogen atoms reacts readily with aldehyde to form the transient intermediate product (VIII) which gives with the elimination of alcohol a tricyclic compound (IX) or (IXa) depending on whether the elimination of alcohol takes place according to **X** or **Y**.

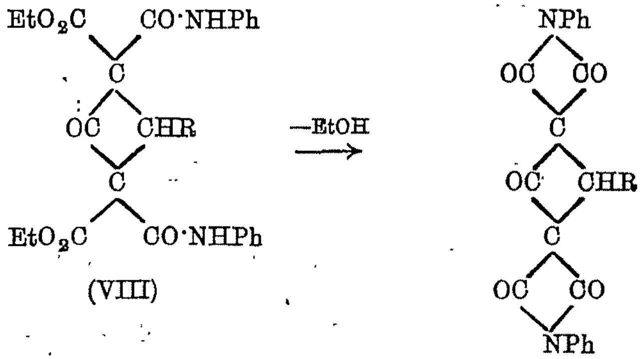


(VIII)



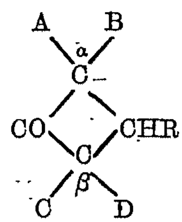
(VIII) (IX)

(Y)



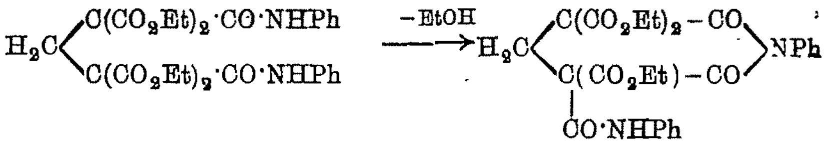
(VIII) (IXa)

The formula (IX) is preferred because a compound having a structure like (IXa), a combination of three four-membered spiro-rings, cannot be expected to be so stable. In accordance with the valency deflexion theory of Thorpe and Ingold (*J. Chem. Soc.*, 1915, **107**, 1080) the formation of the *cyclo*butane ring in compound (VIII) is attended with a widening of the angles α and β between A—B and C—D respectively as the result of which the groupings 'A and C' and 'B and D' come closer together and thus the elimination of alcohol takes place between 'A and C' and between 'B and D'.



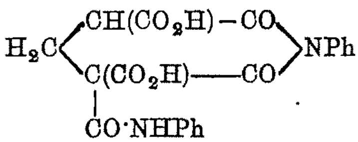
A, D = CO_2Et
B, C = CO·NHPh

The disodium derivative of ethylmethylene dimalonate reacts with phenyl *iso*cyanate to yield the ring compound (X) and not the open-chain diphenylcarbamylmethylene dimalonic ester (Xa) as expected by analogy with compound (VII). This difference is perhaps due to the influence exerted by two pairs of carbethoxy groups in compound (Xa), bringing the two phenylcarbamyl groupings in closer proximity.



(X*a*) (X)

The compound (X) is acidic in nature forming monosodium salt. On mild hydrolysis it yields the compound (XI).

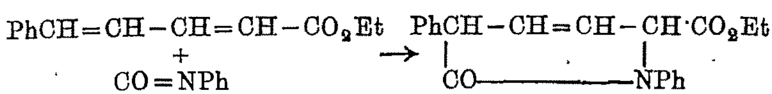


(XI)

Ethyl ketipinate was allowed to react with phenyl *iso*cyanate with the hope that the resulting product will react with aldehydes to yield a compound of the above type (IX). The reaction product could not, however, be obtained in a pure form.

The disodium derivative of ethyl 2:6-diketo-4:4-dimethyl*cyclo*hexane-3:5-dicarboxylate did not react with phenyl *iso*cyanate; the ester was recovered unchanged from the reaction product.

It is worth while mentioning in this connection that an attempt was made to synthesise pyridine derivatives by condensing cinnamylideneacrylic ester with phenyl *iso*cyanate following the method of Diels (*Annalen*, 1925, **443**, 242; 1928, **460**, 98; 1929, **470**, 62), but the condensation, though tried under varying conditions of experiment, did not take place.



Experimental.

Ethyl 2-*phenyliminothiopyran*-4:6-*dione*-3-*carboxylate* (IV, R = Ph).—Sodium (2·3 g.) was gradually added to a solution of ethylacetone dicarboxylate (10·2 g.) in absolute ether (200 c. c.). The

evolution of hydrogen ceased after about 8 hours. The mixture after the addition of phenylmustard oil (7 g.) was allowed to stand overnight. The separated reddish brown precipitate was dissolved in water and acidified with dilute hydrochloric acid, when a brownish semi-solid mass was obtained which crystallised from benzene in colourless rectangular plates, m. p. 128-29° (decomp.), yield 8 g. [Found: N, 4·71; S, 11·04; M. W. (by titration), 298. $C_{14}H_{13}O_4NS$ requires N, 4·81; S, 10·99 per cent. M. W., 291]. It has been found by titration with standard caustic soda solution that it forms a disodium salt. It does not give any disulphide and is not desulphurised by oxide of mercury.

The same compound (IV) was obtained when phenylmustard oil (2 mols.) was allowed to react with ethylacetone dicarboxylate (1 mol.).

Ethyl 2-o-*tolyliminothiopyran*-4:6-*dione*-3-*carboxylate* (IV, R= o-*tolyl*) crystallised from benzene in colourless rectangular plates, m. p. 150° (decomp.). (Found: S, 10·82. $C_{15}H_{15}O_4NS$ requires S, 10·49 per cent).

Ethyl 2-p-*tolyliminothiopyran*-4:6-*dione*-3-*carboxylate* (IV, R= p-*tolyl*) was crystallised from benzene in colourless rectangular plates, m.p. 145° (decomp.). (Found: S, 10·38. $C_{15}H_{15}O_4NS$ requires S, 10·49 per cent).

2-o-*Tolylimino*-4:6-*dione-thiopyran* (V, R=o-*tolyl*).— 4 G. of the compound (IV, R=o-tolyl) were heated under reflux with alcoholic potash (12%) for 8 hours and then diluted with water. The cooled solution, on acidification, gave a solid which crystallised from dilute acetic acid in brownish-white rectangular plates, m.p. 210° (decomp.), yield 2 g. (Found: S, 14·01. $C_{12}H_{11}O_2NS$ requires S. 13·73 per cent). It is readily soluble in dilute alkali and can be precipitated by acids. It does not possess any mercaptanic properties.

2-p-*Tolylimino*-4:6-*dione-thiopyran* (V, R=p-*tolyl*) was crystallised from dilute acetic acid in brownish white rectangular plates, m.p. 214-15° (decomp.). (Found: S, 13·97. $C_{12}H_{11}O_2NS$ requires S, 13·73 per cent).

2-*Phenylimino*-4:6-*dione-thiopyran*-3: 5-*benzylidene* -3-*carboxylate* (VI, R=*phenyl*).—An acetic acid solution of the compound (IV, R= phenyl; 3 g.) and benzaldehyde (1·2 g.) were heated under reflux for about an hour. On cooling, a yellow mass came out which

crystallised from acetic acid in yellowish white rectangular plates, m.p. 274-75°, yield 2·5 g. (Found: S, 8·65. $C_{21}H_{17}O_4NS$ requires S, 8·44 per cent). It is insoluble in alcohol, ether and alkali. The *monosemicarbazone* was obtained as a brownish white crystalline powder by heating the above compound with excess of semicarbazide acetate in dilute acetic acid solution, m.p. above 290°. (Found: N, 12·58. $C_{22}H_{20}O_4N_4S$ requires N, 12·84 per cent).

2-p-*Tolylimino-4: 6-dione-thiopyran-3: 5-benzylidene-3-carboxylate* (VI, R = p-*tolyl*) was crystallised from acetic acid in yellowish white rectangular plates, m.p. above 280°. (Found: S, 7·86. $C_{22}H_{19}O_4NS$ requires S, 8·14 per cent). It is insoluble in alkali.

Ethyl aa'-phenylcarbamylacetone dicarboxylate (VII).—Sodium (2·3 g.) was gradually added to a solution of ethylacetone dicarboxylate (10·2 g.) in absolute ether (200 c c.). After the evolution of hydrogen was over, phenyl *iso*cyanate (12 g.) was added to the solution when at once the reaction began with evolution of heat. The precipitate was filtered overnight, dissolved in water and acidified with dilute hydrochloric acid and the separated solid crystallised from glacial acetic acid in colourless rectangular plates, m. p. 188-89°, yield 15 g. (Found: N, 6·36. $C_{23}H_{24}O_7N_2$ requires N, 6·36 per cent). It is readily soluble in dilute alkali and is precipitated by acids. When it was heated with acetic anhydride for about an hour a clear solution was obtained which, on treatment with sodium carbonate solution, yielded a tarry mass. This yielded a very small quantity of a colourless crystalline product (m.p. 226-27°) on being digested with ether.

Action of benzaldehyde upon compound (VII): *Formation of compound* (XI) (R = Ph).—To a boiling acetic acid solution of the compound (VII, 4·4 g.), benzaldehyde (1·1 g.) was added, the reaction starting at once with evolution of heat. The separated orange yellow crystalline mass crystallised from large quantity of glacial acetic acid in beautiful orange yellow needles, m.p. 247-48° (decomp.), yield 3·5 g. (Found: C, 71·80; H, 4·00; N, 6·58. $C_{26}H_{16}O_5N_2$ requires C, 71·56; H, 3·67; N, 6·42 per cent). It is insoluble in alcohol, benzene and alkali.

The *monosemicarbazone* was obtained in the usual manner and was crystallised from dilute acetic acid in brownish white rectangular plates, m.p. 214-15° (decomp.). (Found: N, 13·77. $C_{27}H_{19}O_5N_5$ requires N, 14·19 per cent).

Action of o-nitrobenzaldehyde upon compound (VII) : *Formation of compound* (IX) (R=*o-nitrophenyl*).—The method of procedure was the same as in the case of the above compound. The product crystallised from large quantity of glacial acetic acid in beautiful orange yellow needles, m.p. 199-200° (decomp.). (Found: N, 8·85. $C_{26}H_{15}O_7N_3$ requires N, 8·78 per cent). It is insoluble in alkali.

a-Phenylcarbamido-aa'a'-tricarbethoxy-N-phenylglutarimide (X) was obtained from ethylmethylene dimalonate and phenyl *iso*cynate exactly in the same manner as in the case of the compound (VII). The precipitate obtained from the reaction product by filtration next day was partly soluble in cold water; the insoluble portion, on crystallisation, was proved to be diphenylurea. The aqueous solution, on acidification with dilute hydrochloric acid, yielded a white precipitate which crystallised from alcohol in beautiful colourless shining needles, m.p. 123-24°. [Found: N, 5·14; M.W. (by titration), 532. $C_{27}H_{28}O_9N_2$ requires N, 5·34 per cent. M.W., 524]. It forms monosodium salt with alkali but is insoluble in sodium carbonate.

Hydrolysis of the compound (X) : *Formation of a-phenylcarbamido-aa'-dicarboxy-N-phenylglutarimide* (XI).—A solution of the compound (X) (4 g.) in *N*-alkali was kept at ordinary temperature for 24 hours and then heated on the water-bath for about half an hour, cooled and acidified with dilute hydrochloric acid when a white precipitate came down. It was purified by precipitation by acid from its solution in sodium bicarbonate. It crystallised from dilute alcohol in colourless plates, m.p. 180° (decomp.), yield 1·5 g. (Found: N, 7·15. $C_{20}H_{16}O_7N_2$ requires N, 7·07 per cent).

Action of phenyl isocyanate upon ketipinic ester.—To an ethereal suspension of the disodium derivative of ketipinic ester (prepared according to the method of Wislicenus, *Ber.*, 1887, **20**, 589) phenyl *iso*cyanate (2 mols.) was added. The reaction mixture, after being allowed to stand overnight, was poured into cold water. The ethereal layer, on evaporation, yielded a white solid which after crystallisation was identified to be diphenylurea. The aqueous layer, on acidification, yielded a very small quantity of a reddish brown tarry mass which could not be purified.

Action of phenyl isocyanate *on ethyl* 2 : 6-*diketo*-4 : 4-*dimethylcyclohexane*-3 : 5-*dicarboxylate.*—The method of procedure was the same as in the previous case. The ethereal layer yielded diphenylurea and the aqueous layer, on acidification, the original ester.

SUMMARY.

1. A thiopyran derivative, obtained by condensing ethylacetone dicarboxylate (1 mol.) with thiocarbimides (1 mol.) reacts with aldehydes to give bridged compounds.

2. Ethyl $\alpha\alpha'$-phenylcarbamylacetone dicarboxylate obtained from ethylacetone dicarboxylate (1 mol.) and phenyl *iso*cyanate (2 mols.) reacts with aldehydes to give tricyclic compounds.

3. Ethylmethylene dimalonate (1 mol.) reacts with phenyl *iso*cyanate (2 mols.) to give α-phenylcarbamido-$\alpha\alpha'\alpha'$-tricarbethoxy-*N*-phenylglutarimide.

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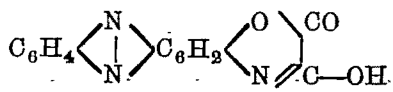
Studies in Heterocyclic Compounds. Part III.

By Anukul Chandra Sircar and Susthir Chandra Sen.

The present investigation, which is a continuation of the work of Sircar and De (*J. Indian Chem. Soc.*, 1926, **2**, 312) and Sircar and Pal (*ibid.*, 1932, **9**, 527) was undertaken with the object of studying how the reactivity of the amino and hydroxy groups in *o*-aminophenol is influenced by the introduction of some compact heterocyclic nucleus in its molecule and also how in compounds containing two dissimilar heterocyclic rings in their molecules the properties of the different heterocyclic nuclei are affected by each other.

2-Hydroxy-3-aminophenazine (Ullmann and Mauthner, *Ber.*, 1902 **35**, 4305) has been chosen as the starting material and it has been found that unlike *o*-aminophenol, it is not so well adapted for the formation of heterocyclic compounds ; evidently the already existing azine ring in the molecule strongly militates against the reactivity of the *ortho*-amino and hydroxy groups. Thus the monoacetyl derivative of 2:3-aminohydroxyphenazine could not be made to eliminate a further molecule of water and close the ring through the free hydroxyl group. Attempts to prepare an oxazole derivative by heating the aminohydroxyphenazine either with glacial acetic acid in presence of sodium acetate or with acetic anhydride under reflux even for 10 hours, were unsuccessful. The desired oxazole formation could only be effected by heating the aminohydroxyphenazine with acetic anhydride under pressure in a sealed tube at 220-30° for about 24 hours, whilst in case of *o*-aminophenol, the oxazole formation can be effected simply by heating it with acetic anhydride for about 7 hours (Ladenburg, *Ber.*, 1876, **9**, 1524). Again all attempts to prepare an oxazole by the action of benzoyl chloride on the aminohydroxyphenazine by following the method of Ladenburg (*loc. cit.*) were unsuccessful, in every case a dibenzoyl derivative being obtained. The desired oxazole could, however, be prepared in the manner described in the experimental.

2:3-Aminohydroxyphenazine has also been condensed with oxalyl chloride. From an examination of the properties of the compound, thus obtained, it is found that the condensation product, instead of existing in the expected diketo form readily, tautomerises to a hydroxyketonic form.



Attempts were next made to condense the aminohydroxyphenazine with malonic and succinic acids in presence of phosphorus pentachloride according to the method indicated by Watson and Mukherjee (*J. Chem. Soc.*, 1916, **109**, 626), but the resulting products resisted all attempts for purification.

When heated in a sealed tube phthalic anhydride condenses with 2:3-aminohydroxyphenazine with the loss of one molecule of water but ring-closure does not take place.

Compounds containing new heterocyclic rings have also been obtained by condensing 2:3-aminohydroxyphenazine with thionyl chloride, potassium ethylxanthate and formic acid. Ring-closure with formic acid was only effected when the acid was absolutely anhydrous and even then it was necessary to heat the mixture in a sealed tube for about 40 hours at 200-30°.

Ethylene dibromide gives a closed ring compound. Though chloroacetyl chloride with *o*-aminophenol forms a closed ring compound (Aschan, *Ber.*, 1887, **20**, 1523) with 2-hydroxy-3-aminophenazine it only attacks the amino group.

Ethyl chlorocarbonate only attacks the amino group of 2:3-aminohydroxyphenazine and no ring formation takes place as in the case of *o*-aminophenol (Grenvik, *Bull. Soc. chim.*, 1877, *ii*, **25**, 177).

Finally 2:3-aminohydroxyphenazine has been condensed with a number of aldehydes such as benzaldehyde, *m*-nitrobenzaldehyde vanillin, salicylic aldehyde, anisic aldehyde, furfural, *o*- and *p*-nitrobenzaldehydes and bromosalicylic aldehyde. As in the condensation of *o*-aminophenol with aldehydes, only the amino group of the hydroxyaminophenazine reacts with the aldehydes.

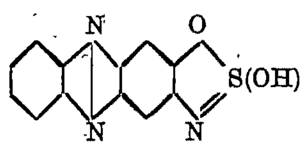
Many of the compounds described in the present paper, through obtained in a pure state, resisted all attempts for crystallisation due evidently to their high molecular complexity. In fact many of them are scarcely soluble in any of the organic solvents.

EXPERIMENTAL.

2-Phenyl-4:5-phenazino-oxazole.—Well powdered 2:3-aminohydroxyphenazine (1 g.) was boiled with benzoyl chloride (20 c.c.) under reflux until a clear solution was obtained. This was then concentrated when yellow needles accompanied by a black tar were obtained. These were filtered from the adhering liquid and washed free from benzoyl chloride with ether and the separated solid was crystallised from toluene (charcoal) and the yellow needles were washed with dilute caustic soda to ensure the removal of benzoic acid. After repeated crystallisation from toluene it was obtained as fine yellow needles, not melting below 300°. It is insoluble in dilute caustic soda or ammonia, readily soluble in hot toluene, glacial acetic acid and strong sulphuric acid (red coloration) and insoluble in alcohol or ether. (Found: N, 14·4. $C_{19}H_{11}ON_3$ requires N, 14·14 per cent).

Phenazinodiketomorpholine. — 2:3-Aminohydroxyphenazine (0·5 g). was boiled with excess of oxalyl chloride (20 c.c.) for about ½ hour. The yellow precipitate was filtered, washed with ether, alcohol and subsequently with dilute hydrochloric acid to remove any unchanged phenazine. It was finally washed with water and dried. On exposure the yellow crystalline powder gradually turns red. It does not melt below 300°. It is insoluble in ether, alcohol or dilute hydrochloric acid, but soluble in ammonium hydroxide, caustic soda and nitrobenzene. It dissolves in strong sulphuric acid with a deep red coloration. (Found: N, 16·04. $C_{14}H_7O_3N_3$ requires N, 15·85 per cent).

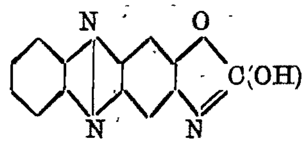
Thiocarboxylaminohydroxyphenazine or Thioxyphenazino-oxazole.



Thionyl chloride (10 c.c.) was added to 2:3-aminohydroxyphenazine (0·5 g.). The mixture immediately turned black and on boiling for about ½ hour under reflux, a part went into solution. This was filtered hot and the filtrate allowed to drop into water when a black microcrystalline powder was obtained which was treated with

dilute hydrochloric acid to remove any unreacted phenazine. The product was then washed with water and dried. It does not melt up to 300°. It is very sparingly soluble in water or dilute hydrochloric acid, moderately soluble in dilute alkalis, alcohol or glacial acetic acid and very soluble in pyridine, nitrobenzene or aniline. It dissolves in sulphuric acid with a greenish yellow coloration which changes to red on dilution. (Found: N, 16·2. $C_{12}H_7O_2N_3S$ requires N, 16·34 per cent).

Carbonylaminohydroxyphenazine (Oxyphenazine-oxazole).



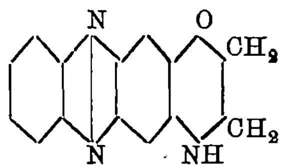
2:3-Aminohydroxyphenazine (0·5 g.) was heated with excess of carbonyl chloride (in toluol solution) on a water-bath under reflux for about 2 hours. The resultant product was then filtered and washed with toluol when a black microcrystalline powder was obtained which on exposure to air turned yellow. It dissolves in most of the organic solvents, *e.g.*, alcohol, acetic acid and nitrobenzene. It is also soluble in caustic soda, ammonia and hydrochloric acid. It does not melt even at 300°. It dissolves in strong sulphuric acid with a red coloration. (Found: N, 18·05. $C_{13}H_6O_2N_3$ requires N, 17·79 per cent).

μ-Suphohydro-4:5-phenazino-oxazole.

An intimate mixture of 2:3-aminohydroxyphenazine hydrochloride (1 g.) and potassium ethylxanthate (0·7 g.) was heated in a sealed tube with alcohol (10 c.c.) at 200-230° for about 10 hours. On opening the tube there was distinct smell of sulphuretted hydrogen. The separated precipitate was repeatedly washed with dilute caustic soda and water to ensure the removal of the parent substances. Finally it was purified by dissolving the substance in strong sulphuric acid and reprecipitating with the addition of water. The black mass obtained was filtered, washed with water and dried. It does not melt below 300°. It is sparingly soluble in alcohol or glacial acetic acid

and moderately so in nitrobenzene and pyridine. It is insoluble in caustic soda or ammonia and dissolves in strong sulphuric acid with a bluish violet coloration. (Found: N, 16·81. $C_{13}H_7ON_3S$ requires N, 16·6 per cent).

Phenazinomorpholine.



2:3-Aminohydroxyphenazine (0·5 g.) and ethylene dibromide (7 c.c.) were sealed together in a tube, thoroughly mixed by shaking and heated for about 12 hours at 180-200°. The product was washed with water, dilute caustic soda and finally with water and dried when a black microcrystalline powder was obtained which did not melt below 300°. It is insoluble in alcohol, ether or dilute caustic soda but soluble in acetic acid. It dissolves in concentrated sulphuric acid with a red coloration but is reprecipitated on the addition of water. (Found: N, 17·5. $C_{14}H_{11}ON_3$ requires N, 17·7 per cent).

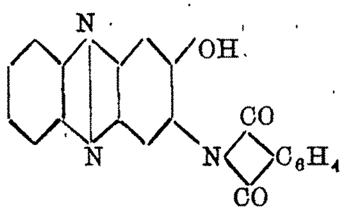
Methylphenazino-oxazole.—Well powdered 2:3-aminohydroxyphenazine (0·2 g.) and acetic anhydride (5 c.c.) were heated together in a sealed tube for about 24 hours at 210-230°. The contents of the tube were diluted with water and the precipitate obtained was washed with water and treated with dilute caustic soda and subsequently with water and dried when a black microcrystalline powder was obtained which did not melt below 300°. It is insoluble in alcohol, ether, nitrobenzene or caustic soda but soluble in acetic acid. It dissolves in strong sulphuric acid with a red coloration but is reprecipitated on addition of water.

This compound is totally different from the mono- and diacetyl compounds obtained by Ullmann and Mauthner (*loc. cit.*) in colour, solubility, m. p. as well as percentage composition of nitrogen. (Found: N, 17·4. $C_{14}H_9ON_3$ requires N, 17·8 per cent).

Phenazino-oxazole.—2:3-Aminohydroxyphenazine (0 2 g.) and formic acid (4 c.c., 100%) were heated in a sealed tube at 280-300° for about 40 hours. The contents of the tube were washed with water, dilute caustic soda and finally with water and dried when a

black microcrystalline powder was obtained, which did not melt below 300°. It is insoluble in alcohol, ether or dilule caustic soda but soluble in acetic acid. It dissolves in concentrated sulphuric acid with a red coloration but is reprecipitated on the addition of water. (Found: N, 18·7. $C_{13}H_7ON_3$ requires N, 19·0 per cent).

Phthalyl 2-Amino-3-hydroxyphenazine.



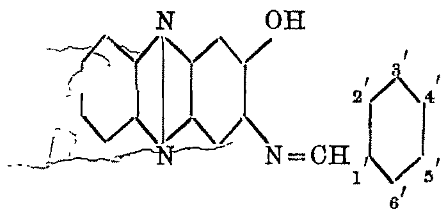
An intimate mixture of 2:3-aminohydroxyphenazine (0·5 g.) and excess of phthalic anhydride (5 g.) was heated in a sealed tube for about 20 hours at 180-200°. The black mass obtained was scraped out and was repeatedly washed with warm soda and finally with water to remove the original starting materials. The black product obtained does not melt up to 300° and cannot be crystallised. It is insoluble in alcohol, ether or nitrobenzene. It is insoluble in caustic soda or ammonia but soluble in acetic acid. It dissolves in concentrated sulphuric acid with a red coloration but is reprecipitated on the addition of water. (Found: N, 12·0. $C_{20}H_{11}O_3N_3$ requires N, 12·3 per cent).

o-*Oxyphenazinourethane*.—2:3-Aminohydroxyphenazine (1 g.) was boiled with ethyl chlorocarbonate (20 c.c.) for about 10 hours on a water-bath under reflux. The chlorocarbonic ester was distilled off and the residue washed with water and boiled. It was then dissolved in hot glacial acetic acid and the filtrate was concentrated until beautiful pale brown plates separated, m. p. 231-32°. It is insoluble in water, alcohol or ether but soluble in hot glacial acetic acid or nitrobenzene. It is moderately soluble in caustic soda. (Found: N, 14·5. $C_{15}H_{13}O_3N_3$ requires N, 14·84 per cent).

Monochloroacetyl 2-amino-3-hydroxyphenazine.—2:3-Aminohydroxyphenazine (0·5 g.) and chloroacetyl chloride (10 c.c.) were heated on a water-bath under reflux for about an hour and the precipitate obtained was washed with alcohol when a black powder was obtained

which turned red on exposure. It was purified several times from boiling alcohol. It dissolves in alcohol, acetic acid, nitrobenzene, caustic soda as also in hydrochloric acid. It does not melt even at 300°. (Found: N, 14·92. $C_{14}H_{10}O_2N_3Cl$ requires N, 14·6 per cent).

* *2-Phenylazomethine-3-hydroxyphenazine.*



2:3-Aminohydroxyphenazine (0·5 g.) was boiled with benzaldehyde (15 drops) in nitrobenzene (30 c.c.) for about 1 hour when a black solution was obtained. This was filtered hot and the filtrate allowed to drop in ether, when a precipitate was obtained. This was filtered and washed repeatedly with ether and alcohol. It was then washed with caustic soda and water and finally obtained as an orange-red microcrystalline powder, not melting at 300°. It is insoluble in water, dilute ammonia, caustic soda, alcohol, glacial acetic acid, dilute hydrochloric or sulphuric acids but is moderately soluble in nitrobenzene. It dissolves in strong sulphuric acid with a red coloration but is reprecipitated on dilution with water. (Found: N, 13·8. $C_{19}H_{13}ON_3$ requires N, 14·05 per cent).

2-(3′-*Nitro*)-*phenylazomethine 3-hydroxyphenazine* was obtained in a similar way to the preceding compound by treating 2:3-aminohydroxyphenazine (1 mol.) with *m*-nitrobenzaldehyde (1 mol.). It is a dark brown powder with no tendency to crystallise or melt. It is insoluble in ether or alcohol but soluble in chloroform, nitrobenzene, pyridine or acetone but moderately soluble in caustic soda and sparingly so in ammonia. It dissolves in strong sulphuric acid with a red coloration. (Found: N, 16·66. $C_{19}H_{12}O_3N_4$ requires N, 16·28 per cent).

* The author was not aware of the work of De and Ghosh (*J. Indian Chem. Soc.*, 1930, 7, 357) until only a few days back. These authors have prepared iminazole by the condensation of benzaldehyde with 9-amino-10-hydroxyphenanthrene. But such ring formation could be effected neither in the case of *o*-aminophenol nor in the case of 2:3-aminohydroxyphenazine, only the amino groups being attacked in these cases.

2-(4′-Hydroxy-5′-methoxy)-phenylazomethine-3-hydroxyphenazine was also prepared in a manner exactly similar to the above with 2:3-aminohydroxyphenazine (0·5 g.) and vanillin (1 g.). It was obtained from glacial acetic acid as a powder which does not melt even at 300°. It is slightly soluble in dilute ammonia or alcohol, fairly soluble in caustic soda and easily soluble in glacial acetic acid. It dissolves in strong sulphuric acid with a dark red coloration which lightens on dilution and the substance is reprecipitated. (Found: N, 12·52. $C_{20}H_{15}O_3N_3$ requires N, 12·17 per cent).

2-(2′-Hydroxy)-phenylazomethine-3-hydroxyphenazine was prepared by condensing 2:3-aminohydroxyphenazine with salicylic aldehyde in a manner similar to the previous compound. It is yellow in colour, lacks any tendency towards crystallisation and does not melt up to 300°. It is insoluble in ether, ammonia or dilute caustic soda, sparingly soluble in alcohol and readily soluble in nitrobenzene. It dissolves in strong sulphuric acid with a dark red coloration which on dilution changes to red and the substance is reprecipitated. (Found: N, 13·6. $C_{19}H_{13}O_2N_3$ requires N, 13·33 per cent).

2-(4′-Methoxy)-phenylazomethine-3-hydroxyphenazine was obtained as a brown microcrystalline powder when 2:3-aminohydroxyphenazine was treated with anisaldehyde as above. It does not melt even at 300° and is insoluble in alcohol and ether, but slightly soluble in caustic soda solution. It is soluble in acetic acid and nitrobenzene. It dissolves in strong sulphuric acid with a violet coloration which changes to yellow on dilution with water. (Found: N, 12·9. $C_{20}H_{15}O_2N_3$ requires N, 12·76 per cent).

2-Furylazomethine-3-hydroxyphenazine was obtained as a brown precipitate with no tendency towards crystallisation from 2:3-aminohydroxyphenazine and furfurol. It does not melt up to 300°. It is insoluble in dilute ammonia, caustic soda or acids but sparingly soluble in alcohol or ether and considerably so in glacial acetic acid or nitrobenzene. It dissolves in strong sulphuric acid with a dark red coloration which changes to red on addition of water and the substance is reprecipitated. (Found: N, 14·84. $C_{17}H_{11}O_2N_3$ requires N, 14·53 per cent).

The following aldehydes also were condensed with 2:3-aminohydroxyphenazine using a slightly different method: (*a*) *o*-nitrobenzaldehyde, (*b*) *p*-nitrobenzaldehyde, (*c*) bromosalicylaldehyde, forming 2-(2′-nitro)-phenylazomethine-3-hydroxyphenazine, 2-(4′-

nitro)-phenylazomethine-3-hydroxyphenazine, 2-(2′-hydroxy-5′ bromo)-phenylazomethine-3-hydroxyphenazine respectively.

The process is to form an intimate mixture of 2 : 3-aminohydroxyphenazine and the aldehydes in a molecular proportion and to heat the mixture in a tube fitted with an air condenser in an oil-bath for about 7 hours at 200-210°. The product was then powdered and washed repeatedly with alcohol, ether, ammonia and finally with boiling water to dissolve out the unreacted starting materials. None of the compounds so obtained melt below 300° and they are almost similar in properties. They are purified by dissolving in boiling nitrobenzene, filtering hot, and precipitating the filtrate with ether.

2-(2′-*Nitro)-phenylazomethine-3-hydroxyphenazine* is a brownish black substance and cannot be crystallised. It is slightly soluble in alcohol and caustic soda but insoluble in ether. It dissolves in strong sulphuric acid with a deep red coloration. On addition of water the substance is reprecipitated. (Found: N, 16·66. $C_{19}H_{12}O_3N_4$ requires N, 16·28 per cent).

2-(4′-*Nitro)-phenylazomethine-3-hydroxyphenazine* was obtained as a brown powder. A very small quantity of the substance was obtained as plates from very highly concentrated nitrobenzene solution but the yield in that case was hopelessly poor. It is insoluble in dilute ammonia, alkalis or acids but slightly soluble in alcohol, moderately soluble in glacial acetic acid and exceedingly soluble in nitrobenzene. It dissolves in concentrated sulphuric acid with a dark red coloration but is reprecipitated on dilution with water. (Found: N, 16·58. $C_{19}H_{12}O_3N_4$ requires N, 16·28 per cent).

2-(2′-*Hydroxy-5′-bromo)-phenylazomethine-3-hydroxyphenazine* is a dark brown uncrystallisable powder and is slightly soluble in dilute ammonia or caustic soda. It is moderately soluble in alcohol or glacial acetic acid and fairly so in nitrobenzene. It dissolves in strong sulphuric acid with a blood red coloration but is reprecipitated on addition of water. (Found: N, 10·8. $C_{19}H_{12}O_2N_3Br$ requires N, 10·66 per cent).

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Action of Alkali on 4-Methyl-$\beta\alpha$-1 :2-naphthapyrone and its 3-Chloro- and 3-Bromo Derivatives. Formation of *cis*- and *trans*-Hydroxy-naphthylcrotonic Acids and a New Naphthylpropionic Aldehyde Derivative.

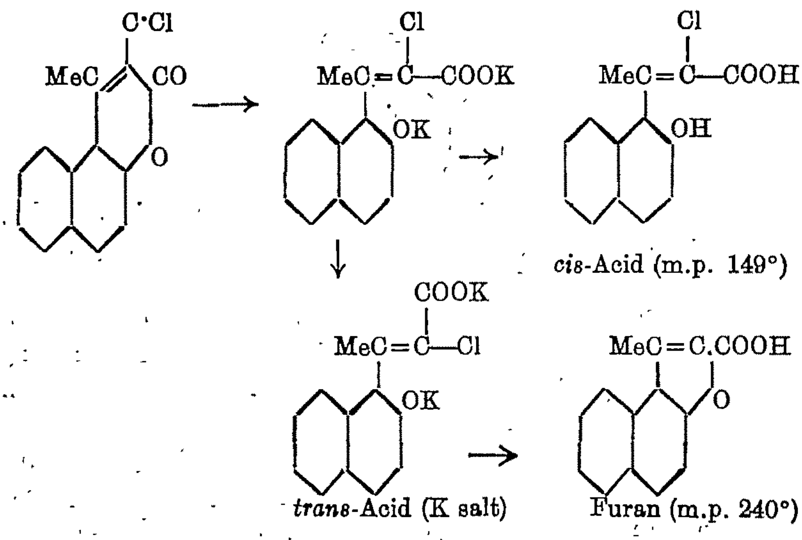
BY B. B. DEY AND A. K. LAKSHMINARAYANAN.

It has been shown (Dey, *J. Chem. Soc.*, 1915, 107, 1630) that 4-methyl-β-naphthapyrone yields on treatment with alkali a fairly stable acid (m. p. 146°) which, on account of the ease with which it could be converted into the original pyrone by such simple methods as treatment of alcoholic solution with HCl gas or crystallisation from boiling solvents, etc., was regarded as having the *cis* configuration. Confirmation of this view has, however, been lacking since all attempts to convert this acid into the *trans* isomer were unsuccessful. We have now succeeded in preparing by the method of boiling an alkaline solution of the pyrone with mercuric oxide (*cf.* Sen and Chakravarti, *J. Indian Chem. Soc.*, 1930, 7, 247 ; Chakravarti, *ibid.*, 1931, 8, 817), a new isomeric acid (m. p. 112°), which, if the previous interpretation was correct, should be assigned the *trans* formula. The latter, however, undergoes conversion into the coumarin practically with the same readiness and in the same characteristic manner as its *cis* isomer, and has, moreover, a lower m.p. —properties which seem to be in conflict with the traditional views regarding the relative stabilities and melting temperatures of *cis*-*trans* isomers. Although the allocation of configurations to the two acids by a comparison of their common physical and chemical behaviours appears thus to be difficult, we have observed an interesting point of difference between them in regard to their response to the stimulus provided by ultraviolet illumination which seems to be highly significant and to justify our previous conclusions. On exposing solutions of the two acids in dry chloroform under identical conditions to the ultraviolet rays of a mercury lamp, it was observed that while the acid (m. p. 146°), believed to have the *cis* structure, remained unaltered, the other isomer was converted to the extent of about 70 % into the naphthapyrone. The assumption which prompted this investigation of the action of ultraviolet light on the two acids was deduced logically from a consideration of the relative

energy contents of a pair of *cis-trans* isomers. If, according to general belief, a *cis* compound existed on a higher energy level than its *trans* isomer, it would be reasonable to expect that the latter could be induced to take up energy, when supplied in a suitable form, and pass into the *cis*-body. The conversion of the *trans* compound into the coumarin is, however, obviously effected through the intermediate *cis*-phase, and the absence of any change in the case of the pure *cis*-acid seems, therefore, to be difficult to understand. The true explanation of this difference would probably be found in the following reasoning. Assuming that the *trans*-acid is converted by an access of energy from the ultraviolet rays into the *cis* condition, it is conceivable that the process would induce an activation of the molecules so as to prevent the transformation from being arrested at this stage but causing it to proceed further until cyclisation to the stable coumarin molecules has been effected. In the case of the *cis*-acid, on the other hand, the non-existence of the initial stimulus or activation may be argued as the cause of the molecules remaining inert and unaltered. Further work in this direction which might help in differentiating between similar pairs of *cis*- and *trans*-acids is engaging our attention.

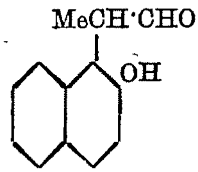
The results obtained from a further study of the action of alkali on the 3-halogeno-β-naphthapyrones have proved to be equally interesting. It was previously reported (Dey, *loc. cit.*) that 3-chloro-4-methyl-β-naphthapyrone reacts with hot alkalis in a manner entirely different from other 3-chlorocoumarins and yields not the expected furan derivative but a stable chlorocoumarinic acid (*cis*). On repeating this work under carefully regulated conditions we find that although the chlorocoumarinic acid is the main but not the sole product under the conditions employed previously, prolonged boiling with concentrated potash does result in the conversion of the major portion of the substance into the hitherto unknown methyl-β-naphthafuran carboxylic acid (m. p. 240°). It may be remarked, however, that the new observation is by no means inconsistent with the assumption previously made that the chloro acid formed in large bulk from the 3-chloro-β-naphthapyrone possessed great stability, though it had the *cis* structure and this rendered the first step to the formation of a furan derivative in this reaction, the elimination of a molecule of alkali chloride from the *trans*-chloro acid, difficult, if not impossible. The present work establishes the point that if the treatment with alkali be continued sufficiently long, a considerable amount of *cis-trans* con-

version actually takes place with the consequent elimination of alkali chloride and closure of the furan ring, thus:

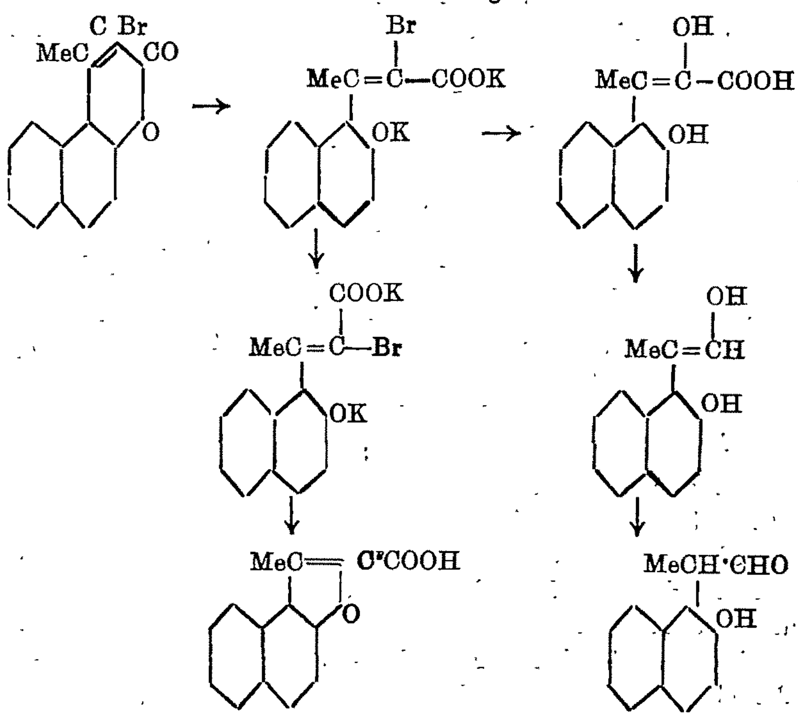


Continuation of work in this field has also served to show that the original anticipation that this singular change of 3-halogeno-β-naphthapyrone into the corresponding coumarinic acid would prove to be general, is incorrect. It has already been shown (Dey, Rao and Sankaranarayanan, *J. Indian Chem. Soc.*, 1933, **10**, 282) that the formation of a stable *cis*-acid is connected, in some way which is not clearly understood yet, with the presence of the methyl group in 4-position, since the unsubstituted 3-chloro- and 5-bromo-β-naphthapyrones yield only the furan derivative unmixed with even a trace of the *cis*-acids. We now find that the substitution of bromine for chlorine, even in the 4-methyl-β-naphthapyrone, leads to results of an entirely different but highly interesting character. No bromo-coumarinic acid could be detected even on boiling with aqueous alkali for a comparatively short period ; on the other hand, considerable quantities of β-naphthafuran carboxylic acid were isolated. But the principal product was a new substance (m. p. 186°) which contained no bromine, dissolved in cold caustic soda and was insoluble in sodium carbonate. It yielded a monoacetyl derivative (m. p. 117°) from which the parent compound was easily regenerated by hydrolysis. The phenolic character of the substance together with the results obtained on analysis led us at first to imagine it to be the 3-hydroxy-4-methyl-β-naphthapyrone produced by the simple replace-

ment of bromine by hydroxyl. A careful examination of the product led, however, to the interesting discovery that it was an aldehyde of the following constitution:

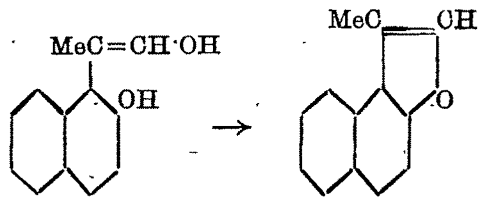


The compound shows all the reducing reactions of aldehydes, yields without difficulty a well-crystallised oxime, a phenylhydrazone and a semicarbazone and is converted by careful treatment with ammoniacal silver oxide into the corresponding acid. The formation of such an interesting product, which we have not observed in any other case although the same reaction was carefully repeated with several other 3-bromo-4-methylcoumarins, can be best explained by the assumption that an intermediate unstable hydroxycoumarinic acid (*cis*) is first produced, and this subsequently loses CO_2 and passes into the hydroxymethylene (enolic) form of the aldehyde. The reactions are indicated in the following scheme:



(m.p. 240°) (m.p. 186°)

"The best confirmatory evidence of the constitution given above is, however, derived from the observation that a practically quantitative conversion of the product into 3-methyl-β-naphthafuran (m. p. 57°) occurs when an alcoholic solution of the aldehyde or of its acetyl derivative is saturated with HCl gas. The following scheme explains the change.



EXPERIMENTAL.

Cis- *and* trans- *Acids from 4-Methyl-β-naphthapyrone.*

cis-β-2-*Hydroxy*-1-*naphthylcrotonic acid* (4-*methyl*-β-*naphthacoumarinic acid*) (Dey, *loc. cit.*).—4-Methyl-1:2-$\beta\alpha$-naphthapyrone (m. p. 178°) (2g.) was dissolved in alcohol (30 c.c.), aqueous caustic potash (20%, 20 c.c.) added and the mixture boiled under reflux for 4 hours. After distilling off most of the alcohol, water (30 c.c.) was added, the solution cooled in ice and acidified with dilute hydrochloric acid. The turbid solution slowly deposited the coumarinic acid in lustrous colourless plates which melted sharply at 146° with evolution of steam and passed into the original naphthapyrone.

trans-β-2-*Hydroxy*-1-*naphthylcrotonic acid* (4-*methyl*-β-*naphthacoumaric acid*).—The pyrone (2 g.) was dissolved in boiling aqueous caustic soda (2 g. in 50 c.c.), the solution diluted with water to 150 c.c. and red mercuric oxide (2 g.) added and the mixture boiled under reflux for 2 hours. On acidifying the cold filtered solution with 2*N*-HCl, it became opalescent and slowly deposited a pale yellow oil which after rubbing for some hours solidified. It dissolved completely in cold sodium bicarbonate, but on acidifying the alkaline solution, the same phenomena of turbidity succeeded by the separation of an oil which gradually solidified were reproduced. The process was repeated thrice when the oil solidified almost immediately and it was finally purified by precipitating its acetone solution with water, yield 1 g. The acid melts sharply at 112° with the sudden evolution of steam and then immediately solidifies. The

residue (m.p. 178°) is found to be identical with 4-methyl-β-naphthapyrone. Attempts to crystallise the acid from hot solvents or to esterify it with alcohol and acid led to its complete conversion into the pyrone. [Found: C, 73·14; H, 5·5; M. W. (by titration with baryta), 227·5. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3 per cent. M. W., 228].

Action of Ultraviolet Rays on the Coumaric and Coumarinic Acids.

(*a*) *Coumaric acid.*—A cold solution of the pure compound (0·5 g.) in dry chloroform (50 c.c.) contained in a quartz flask, to which a drop of a solution of bromine in chloroform (0·05%) had been added, was exposed for 1½ hours to the light from a mercury-arc lamp, the distance being so adjusted as to prevent any appreciable rise of temperature. The solution was allowed to evaporate spontaneously and the residue left in contact with dilute sodium bicarbonate solution for an hour The insoluble residue (0·35 g.) melted at 168-70°, the m.p. rose to 178° by a single crystallisation from acetic acid, and was identified with the β-naphthapyrone. The bicarbonate solution, on acidification with dilute hydrochloric acid, precipitated an oil which soon changed into a solid melting at 110-12°, identical in all respects with the coumaric acid.

(*b*) *Coumarinic acid.*—On exposing a solution of this acid (m.p. 146°) in dry chloroform to the ultraviolet rays of a mercury lamp under precisely similar conditions and evaporating the solvent, a residue completely soluble in cold sodium bicarbonate and recognised by the usual tests to be the unchanged coumarinic acid, was obtained.

Action of Alkali on 3-Chloro-4-methyl-β-naphthapyrone (m.p. 135°): *Formation of 3-Chloro-4-methyl-β-naphthacoumarinic Acid and 3-Methyl-β-naphthafuran Carboxylic Acid.*

(*a*) The chloro derivative (0·5 g.) was boiled with 2*N*-NaOH until it completely dissolved (10 minutes) and the clear yellow solution heated on the water-bath for 1 hour. On cooling and acidifying, colourless glistening plates slowly separated. These were purified by dissolving twice in cold sodium bicarbonate and acidifying, when they melted at 149° simultaneously evolving steam and passing into the chloropyrone.

(*b*) 0·5 G. of the pyrone was boiled with caustic potash solution (20%, 20 c.c.) for 2 hours. On cooling the sparingly soluble K-salt of the naphthafuran carboxylic acid crystallised out. The crystals were dissolved in water and the solution acidified. The pale brown solid which was immediately thrown down was collected and purified by redissolving in sodium bicarbonate and acidifying. Two crystallisations from glacial acetic acid (charcoal) gave colourless needles m. p. 240°. The mother liquor from the pale brown solid, on standing, deposited a small quantity of the impure chlorocoumarinic acid (m. p. 139-40°) which was purified by twice dissolving in cold bicarbonate and acidifying. (Found: C, 73·79; H, 4 80; M. W., 224. $C_{14}H_{10}O_3$ requires C, 74·34; H, 4·42 per cent. M. W., 226). The *ethyl ester* of the naphthafuran carboxylic acid, prepared in the usual manner, crystallises from alcohol in soft colourless needles, m.p. 100°.

3-Bromo-4-methyl-β-naphthapyrone (Bacovescu, *Ber.*, 1910, 43, 1280).—A glacial acetic acid solution of the pyrone (4 g.) was treated with bromine (3 2 g. in 10 c.c.), and the mixture heated on the water-bath until HBr ceased to evolve. The bromo derivative crystallised on cooling and was once recrystallised from acetic acid. The pure product weighed 4 g. (m. p. 145°).

Action of alkali on 3-bromo-4-methyl-β-naphthapyrone: Formation of 3-methyl-β-naphthafuran carboxylic acid and 2-hydroxynaphthyl-1-α-propionic aldehyde.—The bromo compound (3 g.) was boiled with 2*N*-NaOH (40 c.c.) for 1 hour, the cooled alkaline filtrate acidified with 2*N*-HCl and the flocculent yellowish brown precipitate, which had a peculiar odour, was collected and washed with water. It gave no tests for halogen. On leaving in contact with *N*-sodium carbonate solution for sometime only a part of it dissolved, and on acidifying the filtrate, 3-methyl-β-naphthafuran carboxylic acid (m. p. 240°) separated out, yield 0·6 g.

The carbonate-insoluble residue, which formed the main bulk of the precipitate, dissolved in hot water and crystallised on cooling in glistening rectangular plates, m. p. 136°, yield 1 g. It dissolves in cold caustic soda and an alcoholic solution of the substance instantly decolourises cold acid permanganate and readily reduces ammoniacal silver oxide and Fehling's solution on warming. (Found: C, 78·35; H, 5·64. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0 per cent).

The *acetyl* derivative, prepared with acetic anhydride and a drop of pyridine, crystallises from hot water in shining prismatic needles,

m. p. 117°. (Found: C, 74·56; H, 5·58. $C_{15}H_{14}O_3$ requires C, 74·3; H, 5·75 per cent).

The *oxime*, prepared by refluxing an alcoholic solution of the aldehyde with hydroxylamine hydrochloride and potassium hydroxide for 2 hours, crystallises from alcohol in small colourless plates, m. p. 182°. (Found: N, 7·01. $C_{13}H_{13}O_2N$ requires N, 6·51 per cent).

The *phenylhydrazone*, prepared in the usual way, crystallises from acetic acid in clusters of pale yellow needles, m. p 144°. (Found: N, 9·87. $C_{19}H_{18}O\ N_2$ requires N, 9·66 per cent).

The *semicarbazone* forms colourless needles, m. p. 186°. (Found: N, 16·36. $C_{14}H_{15}O_2\ N_3$ requires N, 16·34 per cent).

2-Hydroxynaphthyl-1-*α-propionic acid* was prepared by warming an aqueous solution of the aldehyde with ammoniacal silver oxide on the water-bath, removing the excess of silver with hydrochloric acid and concentrating the filtrate. It crystallises in small needles which readily dissolve in water on warming, m. p. 156°. (Found: Equiv., 220. $C_{13}H_{12}O_3$ requires Equiv., 216).

Action of HCl *gas on an alcoholic solution of* 2-*hydroxynaphthyl*-1-*α-propionaldehyde*: *Formation of* 3-*methyl-β-naphthafuran*.—The aldehyde (1 g.) dissolved in cold absolute alcohol (10 c.c.) was treated with dry HCl gas until saturated and after 12 hours the alcohol was evaporated on the water-bath and the tarry residue repeatedly washed by rubbing with water when it solidified. It was left in contact with dilute NaOH for 1 hour to remove any unchanged aldehyde and then crystallised twice from 50 % alcohol (charcoal), as colourless needles, m. p. 57°. (Found: C, 85·4; H, 5·65. $C_{13}H_{10}O$ requires C, 85·71; H, 5·49 per cent).

The 2-acetoxy derivative, when treated in the same way, gave also a good yield of the naphthafuran.

Attempts were made to condense the aldehyde with acetone, acetophenone and ethyl malonate but without success.

PRESIDENCY COLLEGE,
MADRAS.

Received January 8, 1934.

Reactivity of the Methylene Group in Coumarin-3-acetic Acids. Condensation with Aromatic Aldehydes.

By B. B. Dey and Y. Sankaranarayanan.

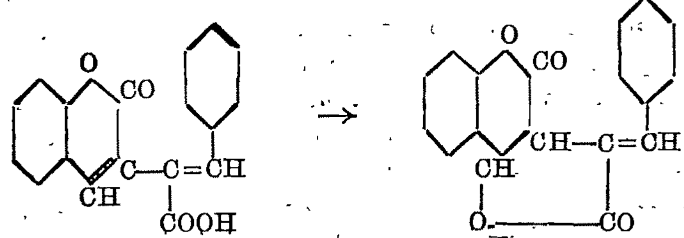
It has been shown that coumarin-4 acetic acids resemble malonic acid in decomposing smoothly and quantitatively into 4-methylcoumarins and carbon dioxide at their melting points, and in having a reactive methylene group (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 107, 277 ; 1925, **2**, 227 ; Dey and Seshadri, *ibid.*, 1931, **8**, 247). Attention was also drawn in the course of these investigations to certain remarkable colour changes which occurred when the products of condensation of a coumarin-4 acetic acid with *p*-hydroxybenzaldehyde or vanillin were treated with alkali and the view was expressed that the phenomenon was presumably due to the facility with which molecules of these compounds could tautomerise into forms which were quinonoid both in the pyrone and in the second benzene nuclei (Dey and Row, *loc. cit.*). A study of the behaviour of similar products obtained from coumarin-3 acetic acids (Dey and Sankaranarayanan, *J. Indian Chem. Soc.*, 1931, **8**, 817) was expected to throw further light on the subject and justify or correct the explanations previously offered.

A comparison of the activities of methylene groups in phenylacetic and coumarin-4 acetic acids has shown the latter to be more reactive, and on grounds similar to those discussed before (*cf.* Dey and Row, *loc. cit.*), it may be argued that the activity of this group in coumarin-3 acetic acids is lower than that in the 4-acetic acids. Thus, while the 4-acetic acids and their ethyl esters condensed easily with aldehydes under the conditions of both the Perkin and the Knoevenagel reactions, coumarin-3-acetic acids could be made to react only by Perkin's method, no condensation occurring when their esters were treated with aldehydes in the presence of piperidine in the usual way. This reduction of activity may be attributed to the influence of the crotonoid system in the coumarin ring, the positive charge of the 4-C atom being expected to strengthen the tendency for ionisation of the CH_2—H atoms, while the potential depletion of

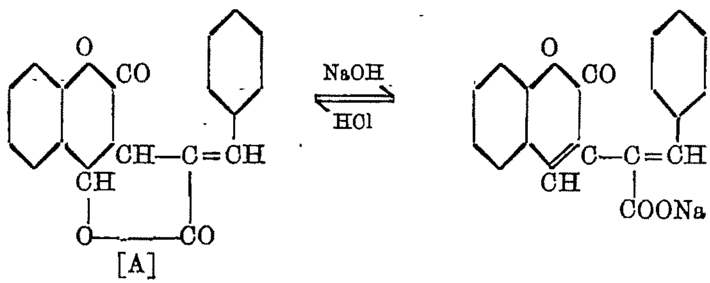
electrons of the 3-C atom might have a feeble inhibiting effect on this tendency (*cf*. Banerjee, *J. Indian Chem. Soc.*, 1931, 8, 777).

The same arguments may be advanced to explain the interesting observation that coumarin-3-acetic acids with a methyl group in position-4, fail to react with aldehydes. The influence of the methyl group is to neutralise the charge of the 4-C atom thus causing a definite and permanent electron deficit in carbon atom-3, and the consequent inhibition of activity of the CH_2 group attached to this atom, These changes seem to provide, therefore, interesting examples of electromeric polarisation resulting from the crotonoid system of the α-pyrone ring.

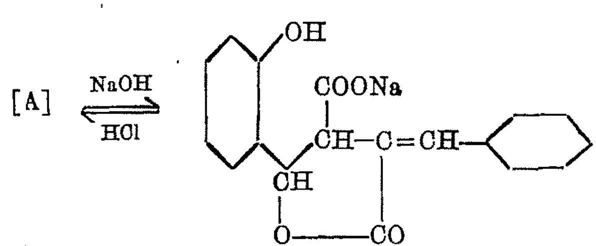
In contrast with the behaviour of the 4-acetic acids which yielded only coumarylphenylethylenes by this reaction, the products obtained from coumarin-3-acetic acids consisted mainly of the ethylene carboxylic acids which suffered little or no decomposition into CO_2 during the process. The compounds, in which the presence of the carboxyl group has been clearly proved, do not, however, dissolve in cold sodium carbonate and attempts to esterify them under the usual conditions were also unsuccessful ; on the other hand, they were readily soluble in cold caustic soda only, unchanged material being precipitated on acidification, and they could be titrated with baryta, the results being in good agreement with the molecular weights of the monocarboxylic acids. An explanation of these interesting observations may be found in the results recently obtained by Linstead (*J. Chem. Soc.*, 1932, 115) from a study of the lactonisation of $\triangle^{\alpha}$- and $\triangle_{\beta}$- unsaturated acids. If we accept his view that these unsaturated acids readily change into lactone systems, the process of lactonisation involving an addition reaction in which the components of the carboxyl group, H and R·CO·O, become attached to the olefinic centre, then these coumarylethylene carboxylic acids having one of the two olefinic bonds in the β-position with respect to the COOH should be capable of lactonising rapidly according to the following scheme:



It is believed, therefore, that the acids exist chiefly in the form of the saturated lactones which are sufficiently stable to resist the action of sodium carbonate but are converted by alkali into the salts of the free acids, from the solutions of which the original lactones only are reprecipitated on acidification, thus:

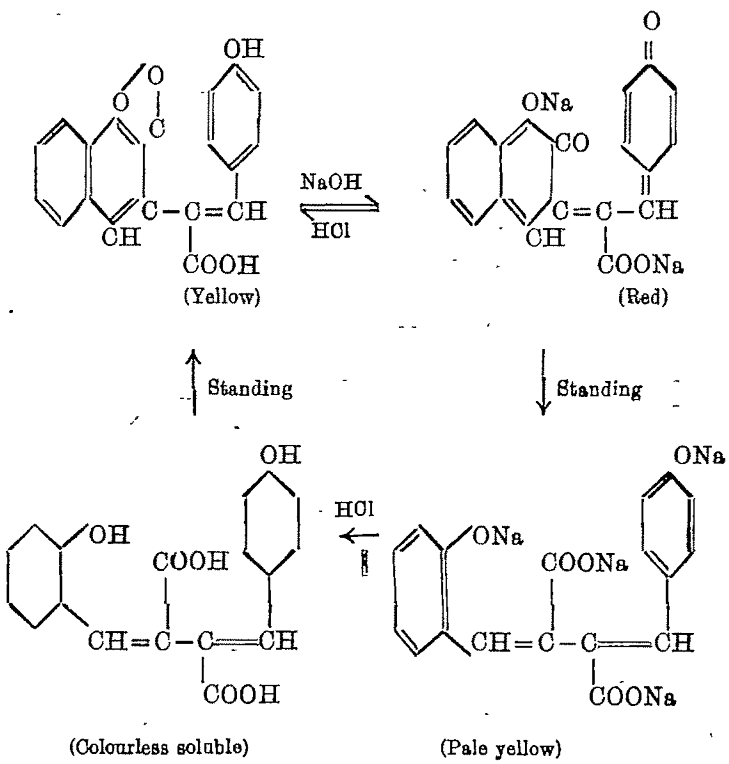


The alternative view that the action of alkalis entails a fission of the pyrone and not of the new lactone ring, as interpreted in the following scheme, is equally plausible.



The products of condensation of *p*-hydroxybenzaldehyde and vanillin with coumarin-3 acetic acids exhibited, contrary to expectation, the same colour changes when treated with alkali, though in a somewhat less intense form, as the analogous products derived from the coumarin-4-acetic acids. They dissolved immediately in cold caustic soda with a vivid red colour which faded rapidly (about 3 minutes) to a pale yellow tint. If the red solution be quickly acidified, the unchanged material is thrown down immediately, while on acidifying the pale yellow solution a white turbidity appeared followed by the slow separation of the original product; these changes are strictly parallel to those observed in the case of the corresponding 4-coumaryl-*p*-hydroxy-

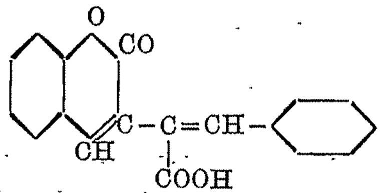
phenylethylene derivatives and are obviously due to the same causes. The *p*-methoxy and *p*-acetoxy derivatives and also the *m*-hydroxybenzaldehyde condensation product, like the corresponding derivatives of coumarin-4-acetic acids, behaved normally and did not exhibit any characteristic changes of colour on dissolution in alkali. We assume, therefore, that the 3-coumaryl-*p*-hydroxyphenylethylene derivatives, like their 4-analogues, tautomerise readily in the presence of alkalis into quinonoid forms which, however, revert to the normal structure through the opening of the pyrone ring by prolonged contact with alkali. The complete cycle of changes would be represented by the following scheme:



It will be seen that the structures suggested for the tautomeric forms of the products in the two cases differ in one respect: while the 4-coumaryl derivative is supposed to become *para*-quinonoid in both the rings (*cf.* Dey and Row, *J. Indian Chem. Soc.*, 1924, **8**, 280), the benzene and the pyrone rings are *para-* and *ortho*-quinonoid respectively in the case of the other product.

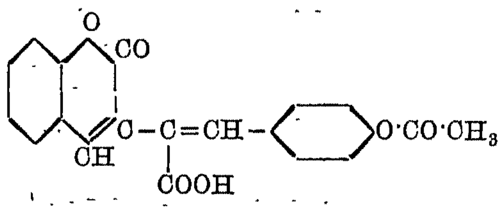
Experimental.

Phenyl-3-coumarylethylene Carboxylic Acid.



The dry sodium salt of coumarin-3-acetic acid (3 g.), freshly distilled benzaldehyde (1·4 g.) and acetic anhydride (12 g.) were heated in a flask under reflux at 160° for 5 hours. The product was thrown into water (100 c.c.), boiled for 5 minutes to decompose the excess of acetic anhydride and the pale red oil which separated was left in contact with water for 12 hours when it solidified to a hard brittle mass. This was crushed with water and purified by reprecipitating from dilute caustic soda. Two crystallisations from alcohol (charcoal) gave colourless tiny plates, m.p. 262°, yield 1·4 g. (Found: C, 73·47; H, 4·35. Equiv., 286·4. $C_{18}H_{12}O_4$ requires C, 73·98; H, 4·11 per cent. Equiv., 292·0).

p-*Acetoxyphenyl-3-coumarylethylene Carboxylic Acid.*



Coumarin-3-sodium acetate (3 g.) and *p*-hydroxybenzaldehyde (1·7 g.) were condensed by heating with acetic anhydride (12 g.) in the usual manner and the solid product obtained by pouring into water was collected and left in contact with dilute alkali for some hours. Most of the substance dissolved leaving a residue (0·3 g. approximately) melting rather indefinitely between 140° and 150°, which was proved to be the decarboxylated product (*vide infra*). The pale yellow filtrate was acidified and the voluminous precipitate collected and crystallised twice from glacial acetic acid in small colourless plates, m.p. 244° (decomp.), yield 1·3 g. (Found:

C, 69·5; H, 4·07. Equiv., 355. $C_{20}H_{14}O_6$ requires C, 68·6; H, 4·0 per cent. Equiv., 350).

p-*Acetoxyphenyl-3-coumarylethylene*.—The small amount of the residue insoluble in alkali obtained from the condensation of coumarin-3-sodium acetate and *p*-hydroxybenzaldehyde was repeatedly crystallised from alcohol in short pale yellow needles, m.p. 165°, yield 0·15 g. (Found: C, 74·5; H, 4·3. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·5 per cent).

p-*Hydroxyphenyl-3-coumarylethylene carboxylic acid* was prepared from the acetoxy compound by boiling with 2*N*-alkali for ½ hour and crystallising the yellow precipitate which was thrown on acidification from boiling methanol as yellow needles, m.p. 272° (decomp.). (Found: C, 70·1; H, 3·92. Equiv., 313. $C_{18}H_{12}O_5$ requires C, 70·1; H, 3·90 per cent. Equiv., 308).

p-*Hydroxyphenyl-3-coumarylethylene* was prepared by the hydrolysis of the acetoxy derivative (m.p. 165°) in the usual way. It crystallised from acetic acid in golden yellow needles, m.p. 227°. (Found: C, 76·8; H, 4·66. $C_{17}H_{12}O_3$ requires C, 77·27; H, 4·54 per cent).

A list of similar compounds prepared by condensing coumarin-3-acetic acids with various aromatic aldehydes under the same conditions is given in the following table.

	Name.	M.p.	Appearance.	Analysis.	Mode of formation.
1.	*m*-Acetoxyphenyl-3-coumarylethylene carboxylic acid	188°	Colourless plates	Equiv., 356·7. $C_{20}H_{14}O_6$ requires Equiv., 350.	Coumarin-3-sodium acetate and *m*-hydroxybenzaldehyde
2.	*m*-Hydroxyphenyl-3-coumarylethylene carboxylic acid	242°	Colourless cubes	...	Hydrolysis of (1)
3.	*m*-Acetoxyphenyl-3-coumarylethylene	140°	Pale yellow plates	C, 74·8; H, 4·4. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·5 %.	By-product in the preparation of 1; insoluble in NaOH
4.	*m*-Hydroxyphenyl-3-coumarylethylene	193°	Colourless rectangular plates	...	Hydrolysis of (3)
5.	3-Coumaryl-3′-methoxy-4′-acetoxyphenylethylene carboxylic acid	207°	Colourless cubes	Equiv., 383·1. $C_{21}H_{16}O_7$ requires Equiv., 380.	Coumarin-3-sodium acetate and vanillin
6.	3-Coumaryl-3′-methoxy-4′-hydroxyphenylethylene carboxylic acid	211°	Yellow cubes	C, 67·4; H, 4·2. $C_{19}H_{14}O_5$ requires C, 67·46; H, 4·14 %.	Hydrolysis of (5); also from coumarin-3-acetic acid and vanillin (Knoevenagel)

	Name.	M.p.	Appearance.	Analysis.	Mode of formation.
7.	3-Coumaryl-4′-methoxyphenylethylene carboxylic acid	225°	Colourless plates	C, 70·5; H, 4·03. $C_{19}H_{14}O_5$ requires C, 70·8; H, 4·35 %.	Coumarin-3-sodium acetate and anisaldehyde
8.	Methylene ether of 3′:4′-dihydroxyphenyl-3-coumaryl ethylene carboxylic acid	270°	Micro-needles	C, 68·4; H, 3·68. $C_{19}H_{12}O_6$ requires C, 67·9; H, 3·57 %.	Coumarin-3-sodium acetate and piperonal
9.	7-Acetoxy-4-methyl-3-coumaryl-3′-coumarin	268°	Colourless prisms	C, 69·0; H, 3·97. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·90 %.	7-Hydroxy-4-methylcoumarin-3-sodium acetate and salicylaldehyde
10.	7:7′-Diacetoxy-4-methyl-3:3′-dicoumarin	220°	Colourless plates	C, 65·32; H, 3·61. $C_{23}H_{16}O_8$ requires C, 65·72; H, 3·81%	7-Hydroxy-4-methylcoumarin-3-sodium acetate and resorcylic aldehyde
11.	7-Acetoxy-4-methyl-3-coumaryl-3′-βα-1:2-naphthapyrone	272°	Rectangular plates	C, 72·3; H, 3·94. $C_{25}H_{16}O_6$ requires C, 72·8; H, 3·85 %.	7-Hydroxy-4-methylcoumarin-3-sodium-acetate and β-naphthol aldehyde
12.	βα-Naphtha-3-coumarylphenylethylene carboxylic acid	253°	Yellow prismatic needles	Equiv., 341·3. $C_{22}H_{14}O_4$ requires Equiv., 342.	βα-1:2-Naphthapyrone-3-sodium acetate and benzaldehyde
13.	3:3′-Di-βα-naphthapyrone	345°	Golden yellow needles	C, 79·27; H, 3·79. $C_{26}H_{14}O_4$ requires C, 80·0; H, 3·59%.	βα-1:2-Naphthapyrone-3-acetic acid and β-naphtol aldehyde

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Formation and Transformation of Carbon Ring Compounds. Part I. Selenium Dehydrogenation of 1 :2 :3 :4-Tetrahydronaphthalene-3 :3-*spiro-cyclo*pentane.

By Suresh Chandra Sen-Gupta.

In recent years a large number of naphthalene and phenanthrene derivatives have been synthesised by the cyclisation of γ-phenyl- and γ-naphthylbutyric acids (Kipping and Hill, *J. Chem. Soc.*, 1899, **75**, 144 ; Krollpfeiffer and Schäfer, *Ber.*, 1923, **56**, 620 ; Schroeter, Müller and Huang, *Ber.*, 1929 **62**, 645 ; Haworth, *J. Chem. Soc.*, 1932, 1125, 2717; Haworth and Bolam, *ibid.*, p. 2248; Haworth, Letsky and Mavin, *ibid.*, p. 1784, 2720). But the effect of various substituents on the ring closure of these γ-phenyl- and γ-naphthylbutyric acids has not as yet been systematically investigated. Thorpe and others (Atwood, Stevenson and Thorpe, *J. Chem. Soc.*, 1923, **123**, 1755 ; Stevenson and Thorpe, *ibid.*, 1922, **121**, 1717; Kon and Stevenson, *ibid.*, 1921, **119**, 88) have only studied the effect of a negative substituent *e. g.*, a carboxyl group on the ring formation of γ-phenylbutyric acids and they had concluded that for facile ring closure the presence of a substituent in the β-position along with a carboxyl group is essential. While Haworth and his co-workers (*loc. cit.*) have cyclised the alkyl derivatives of γ-naphthylbutyric acids to the corresponding ketophenanthrene derivatives.

In the present series of investigation the author, while attempting to synthesise some higher coal-tar hydrocarbons and their derivatives, thou ht it first desirable to make a thorough investigation of the effect of various substituents on the ring closure of γ-phenyl- and γ-naphthylbutyric acids. The influence of *gem*-disubstituents and carbocyclic substituents on the formation of ring compounds from these acids had not been studied previously and first of all specially these types of compounds are being synthesised and their cyclisation studied.

The three well known methods for the ring closure of the γ-substituted butyric acids are as follows :

(*i*) Cyclisation by the action of anhydrous aluminium chloride on the acid chlorides (Kipping, *J. Chem. Soc.*, 1894, **65**, 680; Kipping

and Hill, *loc. cit.*; Kipping and Hunter, *ibid.*, 1901, 79, 602 ; von Braun and Stuckenschmidt, *Ber.*, 1923, **56**, 1724 ; Ruzicka, Ramondt and Wick, *Helv. Chim. Acta*, 1930, **13**, 1117 ; Ruzicka and co-workers, *ibid.*, 1930, **13**, 1402 ; 1932, **15**, 140 ; 1933, **16**, 268, 314).

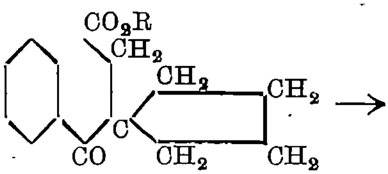
(*ii*) With concentrated sulphuric acid, ring closure takes place generally with a poor yield due to the simultaneous sulphonation of the products (Krollpfeiffer and Shäfer, *loc. cit.*; Atwood, Stevenson, Thorpe and Kon, *loc. cit.*; Shröter, *Ber.*, 1921 **54**, 2243).

(*iii*) Haworth and co-workers (*loc. cit.*) have used 85% sulphuric acid at the temperature of the steam-bath.

In the present investigation 85% sulphuric acid at 100° has been successfully used for the cyclisation of $\beta\beta$-*cyclo*pentane-γ-phenylbutyric acid (II) to form 1-keto-1:2:3:4-tetrahydronaphthalene-3:3-*spiro-cyclo*pentane (III), giving 60% of the theoretical yield. In this case we have got a *cyclo*pentane ring in the $\beta\beta$-position of the γ-phenylbutyric acid and the ring closure proceeds quite satisfactorily. The influence of other carbocyclic groups is also under investigation.

The *spiro*-hydrocarbon, 1:2:3:4-tetrahydronaphthalene-3:3-*spiro*-*cyclo*pentane (IV) obtained by the reduction of the above keto compound (III) exhibited most interesting ring transformation on selenium dehydrogenation and furnished phenanthrene and anthracene by a vicinal or angular recombination after the opening up of the *cyclo*pentane ring. The *cyclo*pentane ring was not dehydrogenated till it opened up and was transformed to a six membered ring. Similar observation regarding failure to dehydrogenate a five membered ring had been made by Ruzicka and Thomann (*Helv. Chim. Acta*, 1933, **11**, 224). Clemo and Ormston (*J. Chem. Soc.*, 1932, 1781) indicate the probability of similar ring transformation of 1-keto*cyclo*hexane-2: 2-*spiro-cyclo*pentane (VII) by selenium dehydrogenation to naphthalene, though they had not practically verified it. This observation of the ring transformation of the *spiro*-hydrocarbon (IV) is of importance considering the present view of the structure of the sterols and bile acids, which are considered as containing a phenanthrene ring in the molecule. This view, however, follows from the fact that the Diels's hydrocarbon (Diels, Gadke and Körding, *Annalen*, 1927, **459**, 1), obtained by the selenium dehydrogenation of the sterols and bile acids, had been formulated to be a phenanthrene derivative (Rosenheim and King, *Chem. Ind.*, 1932, **51**, 464; Wieland and Dane, *Z. physiol. Chem.*, 1932, **210**, 268). Even if

Diels's hydrocarbon be a phenanthrene derivative (Ruzicka, Ehmann, Goldberg and Hösli, *Helv Chim. Acta*, 1933, **16**, 833; Kon, *J. Chem. Soc.*, 1933, 1081; Cook and Hewett, *ibid.*, 1933, 1098) it cannot be definitely concluded that this phenanthrene ring structure is also pre-existent in the sterols and bile acid molecules. It is not improbable that a naphthalene-*spiro*-*cyclo*pentane ring is present in the molecule which during selenium dehydrogenation forms a phenanthrene derivative.



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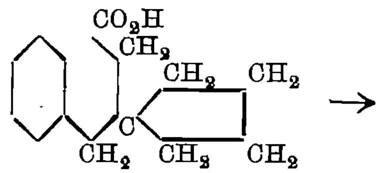

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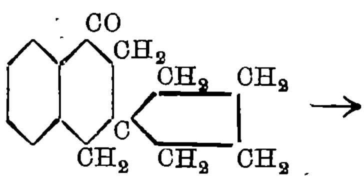

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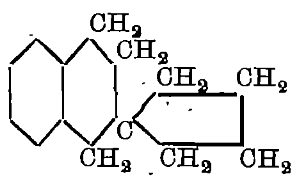

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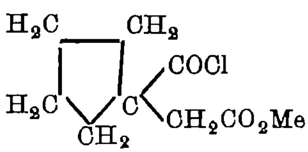

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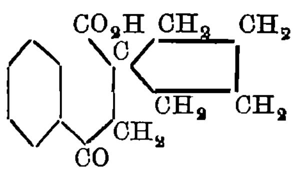

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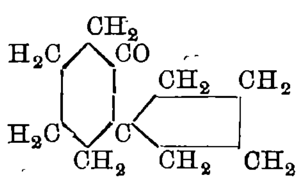

(VII)

For the synthesis of $\beta\beta$-*cyclo*pentane-γ-phenylbutyric acid, the method for the synthesis of γ-substituted butyric acids by the action

of the anhydrides of substituted succinic acids on aromatic compounds has been utilised (Borsche and Saurenheimer, *Ber.*, 1914, **47**, 1645; Mayer and Stamm, *Ber.*, 1923, **56**, 1424; Haworth and co-workers, *loc. cit.*; Oppenheim, *Ber.*, 1901, **34**, 4228).

The anhydride of *cyclo*pentane-1-carboxy-1-acetic acid (Bardhan, *J. Chem. Soc.*, 1928, 2599) was condensed with benzene in presence of anhydrous aluminium chloride, giving *cyclo*pentane-1-benzoyl-1-acetic acid (I, R=H). That the reaction does not proceed in the alternative way, giving *cyclo*pentane-1-acetophencne-1-carboxylic acid (VI), follows from the synthesis of the keto acid (I) by the following unambiguous method. The acid chloride of the methyl acid ester of *cyclo*pentane-1-carboxy-1-acetic acid, having the constitution represented by formula (V) (Bardhan, *loc. cit.*) reacts with benzene in presence of aluminium chloride giving the methyl ester of *cyclo*pentane-1-benzoyl-1-acetic acid (I, R=Me), which on hydrolysis gave *cyclo*pentane-1-benzoyl-1-acetic acid (I, R=H). This keto acid on reduction by Clemmensen's method (Clemmensen, *Ber.*, 1913, **46**, 1837) gave *cyclo*pentane-1-benzyl-1-acetic acid (II), which on cyclisation with 85% sulphuric acid gave 1-keto-1:2:3:4-tetrahydronaphthalene-3:3-*spiro-cyclo*pentane (III), this on reduction by Clemmensen's method gave 1:2:3:4-tetrahydronaphthalene-3:3-*spiro-cylo*pentane (IV). Selenium dehydrogenation of this *spiro*-compound at 300-50° gave mainly phenanthrene and a little anthracene.

Most interesting results are expected by the selenium dehydrogenation of the corresponding *spiro-cyclo*hexane compounds and investigations in that d'rection are in progress.

Experimental.

cyclo*Pentane*-1-*benzoyl*-1-*acetic acid* (I, R=H).—(*a*) Powdered aluminium chloride (27 g.) was slowly added to a mixture of benzene (35 c.c.) and the anhydride of *cyclo*pentane-1-acetic-1-carboxylic acid (31 g.) (Bardhan, *loc. cit.*) cooled in ice-water. Hydrogen chloride was evolved at the ordinary temperature. The mixture was allowed to stand overnight and the reaction completed by warming the mixture on the water-bath at 60-65° for 3 hours. The viscous brown product was treated with ice and dilute hydrochloric acid and the excess of benzene removed by steam distillation. The white solid was collected, washed with dilute hydrochloric acid, extracted with hot sodium carbonate solution and precipitated with

dilute hydrochloric acid. The acid was crystallised from rectified spirit as white plates, m.p. 165-66°, yield 28 g. (Found: C, 72·2; H, 6·8, $C_{14}H_{16}O_3$ requires C, 72·4 ; H, 6·9 per cent).

The *semicarbazone*, prepared in the methyl alcoholic solution in the usual manner, crystallised from rectified spirit, m.p. 162° (decomp.). (Found: C, 62·0; H, 6·4. $C_{15}H_{19}O_3N_3$ requires C, 62·2 ; H, 6·6 per cent).

(*b*) Powdered aluminium chloride (6 g.) was slowly added to a mixture of excess of benzene (20 c.c.) and the acid chloride of the methyl acid ester of *cyclo*pentane-1-acetic-1-carboxylic acid (7·3 g.), cooled in ice water. The mixture was allowed to stand overnight and then heated to 60-65° for 3 hours, decomposed with ice and dilute hydrochloric acid and the excess of benzene distilled off in steam. The residual oil was extracted with ether, the ether extract washed with soda solution, dried, ether removed and the keto-ester distilled at 182-83°/5mm. as a thick oil which readily solidified, m.p. 39-40°. (Found: C, 72·9 ; H, 7·0. $C_{15}H_{18}O_3$ requires C, 73·2 ; H, 7·3 per cent). The ester was hydrolysed with alcoholic potash, the alcohol distilled off, residue dissolved in water and on acidification with dilute hydrochloric acid the acid separated out, which was crystallised from spirit, m.p. 165-66°, the mixed m.p. with the keto acid prepared by method (*a*) was not depressed.

cyclo*Pentane*-1-*benzyl*-1-*acetic acid* (II).—The previous keto acid (35 g.), amalgamated zinc (175 g.) and concentrated hydrochloric acid (175 c.c.) were allowed to stand at the ordinary temperature for 3 hours and then boiled for 18 hours. After cooling the acid was filtered, dissolved in boiling sodium carbonate solution, acidified with hydrochloric acid and the white precipitated acid crystallised from dilute alcohol as fine long needles, m.p. 99-100°, yield 25 g. (Found: C, 76·8 ; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·0 ; H, 8·2 per cent.).

1-*Keto*-1 :2 :3 :4-*tetrahydronaphthalene*-3 :3-spiro-cyclo*pentane* (III).—The foregoing acid (18 g.) was slowly added to a mixture of concentrated sulphuric acid (54 c.c.) and water (18 c.c.) and heated on the steam bath for 1½ hours., diluted with ice water and the separated oil extracted with ether, washed with dilute ammonia, dried, ether removed and distilled under reduced pressure. It is a thin colourless oil having a characteristic smell, b.p. 140-41°/4mm., yield 10 g. (Found: C, 83·9 ; H, 8·0. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0 per cent).

The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 173-74°.

1:2:3:4-*Tetrahydronaphthalene*-3:3-spiro-cyclo*pentane* (IV).—The former *spiro*-keto compound (9 g.), amalgamated zinc (50 g.) and concentrated hydrochloric acid (50 c.c.) were boiled for 24 hours, diluted with water, extracted with ether, the ether solution washed, dried, ether removed when the residue distilled at 113-14°/4 mm. as a colourless oil (5 g.) and a little unreduced keto compound (1g.) having a higher b.p. (Found: C, 90·1 ; H, 9·7. $C_{14}H_{18}$ requires C, 90·3 ; H, 9·7 per cent).

1:2:3:4-Tetrahydronaphthalene-3:3-*spiro*-*cyclo*pentane (3 g.) was heated with selenium (7 g.) in a metal-bath at 300-350° for 40 hours. The product was repeatedly extracted with ether, ether removed, and the residual oil distilled over sodium under reduced pressure; the first part a liquid distillate (A) contains phenanthrene and some undehydrogenated product and the second fraction (B) which solidifies in the side tube of the distilling flask contains mixture of phenanthrene and anthracene. The fraction (A) was treated with alcohol and picric acid and the separated yellow picrate was recrystallised from alcohol. On decomposing this picrate with dilute ammonia a solid hydrocarbon was obtained which was crystallised from alcohol and identified as phenanthrene, m.p. and mixed m.p. with an authentic sample of phenanthrene was 100°. (Found: C, 94·3 ; H, 5·6. $C_{14}H_{10}$ requires C, 94·4 ; H, 5·6 per cent). The m.p. of the picrate and the mixed m.p. with an authentic sample of the picrate of phenanthrene was 145°.

The fraction (B) was dissolved in a little warm benzene and allowed to crystallise. the first crop was collected and recrystallised from benzene ; this was identified as anthracene, m.p. and mixed m.p. with an authentic sample of anthracene was 213°.

The author desires to express his thanks to Dr. P. Neogi and Dr. M. Q. Khuda for the kind facilities they have given for carrying on this work and to Dr. J. C. Bardhan for his kind help and interest in this investigation.

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Indigoid Vat Dyes of the Isatin Series. Indole-thionaphtheneindigos.

By Sisir Kumar Guha and Hari Prasad Basu-Mallik.

In view of the observation made by one of us (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 680) that the scarlet-red shades obtained from 2-(5-methyl)-thionaphthene-acenaphthyleneindigo and its halogen derivatives on cotton as well as on wool are deeper than those obtained from Ciba scarlet-G and its halogen derivatives (Guha, *ibid.*, 1932, **9**, 423), it appeared of interest to make a systematic study of similar vat dyes in the isatin series as 3-indole-2′-thionaphtheneindigo (Bezdzik and Friedlander, *Monatsh.*, 1908, **9**, 376 ; E. P. 17162/06) and its dibromo derivative (E P. 6490/07) have received technical application under the name of Thioindigo scarlet-R and Ciba red-G respectively.

With this object in view, isatin and its various derivatives were condensed with 5-methyl-3-hydroxythionaphthene (Auwers and Arndt, *Ber.*, 1909, **42**, 541) and the following compounds prepared: 3-indole-, 3-(5-chloro)- indole-, 3-(5-bromo)-indole-, 3-(5-iodo)-indole-, 3-(5 : 7-dibromo)-indole-, 3-(5-bromo-7-nitro)-indole-, 3-(5 : 7-dinitro)-indole-2′-(5′-methyl)-thionaphtheneindigo. It was noticed in every case that condensation proceeded with the greatest ease and the products separated rapidly in well-defined crystalline form. They are all soluble in pyridine with magenta red colour, soluble in aniline and nitrobenzene ; except the first named compound, which is moderately soluble in alcohol, the rest are very sparingly soluble in the same solvent. When heated above 310°, these dyes melt and quickly volatilise evolving coloured vapours of the respective substances which deposit again as pure dyes (*cf.* Guha, *loc. cit.*).

These indigoid dyes dye wool evenly from an acid bath when freshly precipitated by water from the concentrated sulphuric acid solution in which they dissolve producing characteristic coloration. All of them, excepting the dinitro compound which forms a yellow vat, yield light yellow vat by means of alkaline hydrosulphite and

from it the dye is reprecipitated when exposed to air. The compounds described, are arranged above according to the gradual increase of the depth of the shades of the dyes obtained on wool as well as on cotton. Of the scarlet-red shades obtained from the first four substances, the one that is obtained from the iodo compound is the deepest. The dibromo derivative produces a deep red shade. The bromonitro and the dinitro compounds give rise to dark red shades and the shade obtained from the latter is the deeper of the two. It has also been found that the scarlet red shades obtained from the indigoid dyes derived from isatin, its 5-chloro and 5-bromo derivatives are distinctly deeper than those obtained from the nearly corresponding dyes in the acenaphthenequinone series (Guha, *loc. cit*).

Finally, for the purpose of comparison of dyeing shades on wool and on cotton, the analogously composed 2-(5-methyl)-thionaphthene-9′-phenanthreneindigo was prepared. This substance is dark chocolate, it dyes wool in brown shades from an acid bath and dyes cotton in dull brown colour from a yellow alkaline hydrosulphite vat.

It has been assumed that the β-ketonic group in isatin and its various derivatives takes part in the reaction from the analogy of the constitution of the similar compound, 3-indole-2-thionaphthene-indigo and its dibromo derivative (*loc. cit.*).

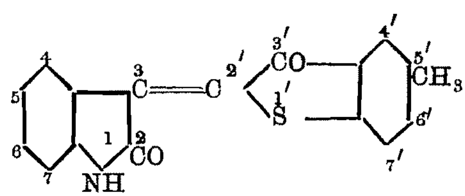
EXPERIMENTAL.

5′:7-Dinitroisatin.—In preparing this substance we have employed the following modification of Menon, Perkin and Robinsons' method (*J. Chem. Soc.*, 1930, 840) which also gave pure and almost quantitative yield. To a solution of powdered isatin (2·5 g.) in strong sulphuric acid (*d* 1·84, 25 c.c.) cooled to 0°, finely powdered potassium nitrate (25 g.) was added in small quantities at a time, keeping the temperature within 15° and the mixture stirred thoroughly. The resulting thick brownish-yellow mixture was allowed to attain room temperature and then heated on a water-bath at 50-55° with continuous stirring. After one hour canary yellow precipitate began to separate, the heating was continued for 2 hours more when the separation was almost complete; the mixture poured into crushed ice with stirring and allowed to stand overnight in a cooled chamber and filtered ; the residue on the filter paper was washed well with

ice-cold water and dried. It was finally crystallised from xylene in prisms, m. p. 209-10° yield 2·8 g.

It is readily soluble in pyridine, acetone, ethyl acetate; soluble in acetic acid, alcohol, amyl alcohol, xylene and in hot water; sparingly soluble in chloroform, benzene and ether; insoluble in ligroin and carbon tetrachloride.

3-Indole-2′-(5′-methyl)-thionaphtheneindigo.



Isatin (0·294 g.), dissolved in boiling glacial acetic acid, was mixed with 5-methyl-3-hydroxythionaphthene (0·328 g.) in hot acetic acid (10 c.c.). The resulting red-brown solution, on treatment with a small quantity of strong hydrochloric acid and shaking turned dark red (almost black) and silky scarlet red beautiful needles separated. The mixture was boiled for 15-20 minutes to complete the reaction, filtered while still hot, washed with acetic acid and with hot water. It was purified by heating with 50% acetic acid and finally crystallised from acetic acid in fibre-like silky scarlet red needles. The substance is soluble in chloroform, acetone, acetic acid, toluene and less so in benzene; sparingly soluble in carbon tetrachloride and ligroin. Strong sulphuric acid dissolves it with olive brown coloration. It dyes wool in brilliant and pleasant scarlet red shade from an acid bath and dyes cotton in light red shade from an alkaline hydrosulphite vat at 50-60°. Attempts to dye cotton from cold hydrosulphite vat in order to obtain the desired deep scarlet red shade were not, however, met with success (*cf.* 3-indole-2′-thionaphtheneindigo, Rowe, *Colour Index* No. 1225, 1924 edition). (Found. S, 11·19. $C_{17}H_{11}O_2NS$ requires S, 10·92 per cent).

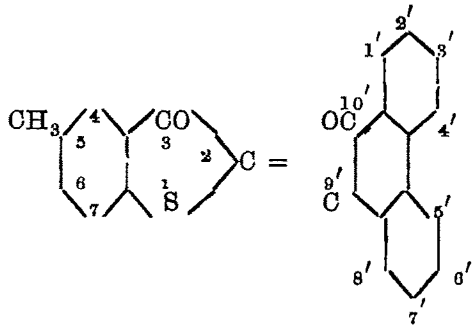
The indole-thionaphtheneindigos described in Table I were prepared in a similar way. They were purified by boiling with alcohol and finally crystallised from pyridine, washed with dilute hydrochloric acid, hot water and dried at 150°.

Table I.

T = Thionaphtheneindigo, m = 5-methyl-3-hydroxythionaphthene.

Name.	Mol. Formula.	Method of preparation.	Appearance.	Solubilities.	Colour in strong H_2SO_4.	Shade on wool from acid bath.	Shade on cotton from hydrosulphite vat.	Analysis Found.	Calc.
(1) 3-(5-Chloro)-indole-2′-(5-methyl)-T	$C_{17}H_{10}O_2NClS$	5-Chloro-isatin + m	Silky scarlet-red small needles	Difficultly soluble in amyl alcohol, xylene, acetic acid; sparingly soluble in chloroform, benzene, acetone	Olive green	Scarlet red.	Scarlet red.	Cl, 10·63	10·88
(2) 3-(5-Bromo)-indole-2′-(5′-methyl)-T	$C_{17}H_{10}O_2NBrS$	5-Bromo-isatin + m	Silky scarlet-red fibre-like needles	Do	Do	Do	Do	Br, 21·85	21·51
(3) 3-(5-Iodo)-indole-2′-(5′-methyl)-T	$C_{17}H_{10}O_2NIS$	5-Iodo-isatin + m	Deep scarlet-red silky needles	Do	Do	Deep scarlet red	Deep scarlet red	I, 30·24	30·31
(4) 3-(5:7-Dibromo)-indole-2′-(5′-methyl)-T	$C_{17}H_9O_2NBr_2S$	5:7-Dibromoisatin + m	Deep red fibre-like clusters of silky needles	Sparingly soluble in amyl alcohol, acetic acid, benzene, xylene	Do	Deep red	Deep red	Br, 35·82	35·47
(5) 3-(5-Bromo-7-nitro)-indole-2′-(5′-methyl)-T	$C_{17}H_9O_4N_2BrS$	5-Bromo-7-nitroisatin + m	Dark red small needles	Sparingly soluble in chloroform, amyl alcohol, benzene, acetic acid, acetone	Deep green	Dark red	Dark red	Br, 19·58	19·18
(6) 3-(5:7-Dinitro)-indole-2′-(5′-methyl)-T	$C_{17}H_9O_6N_3S$	5:7-Dinitro-isatin + m	Dark red glistening needles	Sol. in xylene; difficultly sol. in acetic acid, acetone, chloroform and benzene	Deep green	Dark red	Do	S, 7·97	8·35

* 2-(5-*Methyl*)-*thionaphthene*-9'-*phenanthreneindigo*.



The dye is soluble in amyl alcohol, xylene, pyridine, aniline and nitrobenzene ; moderately in chloroform, acetic acid and benzene; sparingly soluble in acetone, and alcohol; strong sulphuric acid dissolves it with reddish-brown coloration. (Found: S, 8·86. $C_{23}H_{14}O_2S$ requires S, 9·04 per cent).

We thank Dr. K. S. Caldwell B.Sc., Ph. D., Principal, Science College, Patna, for taking interest during the progress of this work.

SCIENCE COLLEGE,
PATNA (B. & O.).

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* The compound was prepared by methods already described from phenanthraquinone (0·416 g.), methyl hydroxythionaphthene (0·328 g.) in glacial acetic acid solution with traces of hydrochloric acid and purified as usual, m.p. 300°.

The Synthesis of o-Aldehydocarboxylic Acids.

By John H. Gardner.

In a recent paper, Chakravarti describes as a general method for the synthesis of substituted phthalaldehyde acids, the oxidation of symmetrically substituted naphthalene derivatives to phthalonic acids followed by the decomposition of the latter to the phthalaldehyde acids (Chakravarti, *J. Indian Chem. Soc.*, 1933, **10**, 693). As a specific example, he described in detail the preparation of 5-methoxyphthalaldehyde acid from 2:6-dimethoxynaphthalene. Since this work is very close to some investigations which have been carried out in this laboratory, some of which have been published, it was thought desirable to report some of our results at this time. I wish to state explicitly that there is no intention of disputing Chakravarti's priority in demonstrating that this method is of general application.

As a preiliminary study, the oxidation of α-methoxynaphthalene was studied. While it was expected that the main product would be phthalonic acid, it was hoped that the ring bearing the methoxyl group would be sufficiently resistant to oxidation to permit of the formation of some methoxyphthalonic acid. However, when a solution of the oxidation product was treated with aniline, the aniline condensation product of phthalonic acid was obtained in good yield and purity. Its identity was confirmed by conversion to the aniline derivative of phthalaldehyde acid. There was no evidence of the presence of any methoxyphthalonic acid.

Later, 3:5-dimethoxynaphthalene was oxidised in a similar way with alkaline permanganate. 3-Methoxyphthalonic acid was formed as was shown by its conversion to 3-methoxyphthalaldehyde acid (Naylor and Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4109). As this work has already been published elsewhere, it will not be repeated here.

Experimental.

Oxidation of α-methoxynaphthalene.—α-Methoxynaphthalene (39·5g.) was suspended in 0·5*N*-sodium hydroxide (500 c. c.). A hot

solution of potassium permanganate (212 g.) in water (1500 c.c.) was added during 1½ hours. The mixture was boiled for ½ hour after the last addition of permanganate. Ethyl alcohol was added to decompose any remaining permanganate. The solution was cooled and filtered. The filtrate was acidified with hydrochloric acid and evaporated to 500 c.c. Aniline (100 c.c.) was added and the mixture was heated on the water-bath for 1½ hours. It was then filtered. There was precipitated 39 g. of the aniline derivative of phthalonic acid, m.p. 159-60° (decomp.), after crystallisation from alcohol.

Decomposition of the aniline derivative of phthalonic acid.—A suspension of the aniline derivative of phthalonic acid (28 g.) in sodium-dried xylene (190 c.c.) was boiled for 1½ hours. After cooling the solid precipitate was filtered out, yield 10 g., m.p. 175-76° after crystallisation from alcohol. A mixed melting point with the aniline derivative of phthalaldehyde acid (m.p. 176-77°) melted at 176-77°, showing that the materials were identical.

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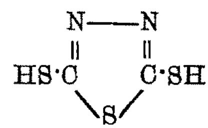
Received April 28, 1934.

A Note on the Use of Dimercaptothiobiazole as an Analytical Reagent.

By Jagannath Gupta.

Dimercaptothiobiazole 

has been found to be a very convenient reagent for the estimation of copper, lead and bismuth, and for their separation from the metals of the II A and the rest of the analytical groups (As, Sb, Sn, Mo, Fe, Zn, etc.). The substance serves also as a very sensitive micro-reagent for Cu and Bi. This work was completed in this laboratory by the end of December, 1933, under the guidance and suggestion of Prof. P. R. Ray and is now ready for submission as a part of my thesis for the ensuing M.Sc. examination in July.

In the meantime a paper by Dubsky and Okâc on " Qualitativer Nachweis des Wismuts mit schwefelhaltigen organischen Reagenzien—1. Nachweis mit Dimercaptothio-diazol " has appeared in the *Z. anal. Chem.*, **96**, (1934), 267. As our work cannot be published before my examination is over, it is necessary that a short note should now be communicated, though not with any intention of claiming priority so far as the reaction for Bi is concerned, but simply as a justification of our independent work in connection with Bi and as a reservation of our right with reference to Cu and Pb.

Copper has been separated in dilute acid solution from Zn, Mn, Ni, Co, Mo, Wo and Fe (in the ferrous state by treatment with SO_2), from As and Sn^{4+} in tartaric acid solution, and from Sn and Sb in the presence of sodium fluoride. Lead has been separated from Sn^{4+} in presence of tartaric acid, and from As, Sb and Sn in presence of tartaric acid and sodium fluoride. A similar separation has also been effected in the case of bismuth.

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Received May 9, 1934.

REVIEW

Essai sur la Chimie Comparié—Les corps simples—by Dr. I. N. Longinescu, Paris:. Published by Les Presses Universitaires de France 1932.

The author considers that in the study of inorganic chemistry insufficient attention has been paid to the relations among the members of the groups of the periodic system and hence attempts to fill up the deficiency. Undoubtedly the comparative treatment is advantageous and this small treatise may be locked upon as a good supplement to the existing works. Ephraim's Anorganische Chemie is planned on the same line.

Prof. Longinescu's second volume dealing with the binary compounds based on the same principle is awaited with interest.

P. B. S.

SIR P. C. RAY SEVENTIETH BIRTHDAY

COMMEMORATION MEDAL

Applications are invited for the above medal from young Indian Chemists below thirty years of age for the best single original contribution published in the Journal of the Indian Chemical Society during 1934. The relevant rules are given below.

The award for 1933 has been made in favour of Mr. S. K. Ray for his work on "Studies on Polyhalides."

P. RAY,
Hony. Secretary,
Indian Chemical Society.

RULES

1. The medal will be awarded annually for the best original paper (single and not joint) on any subject in Chemistry published in the Journal of the Indian Chemical Society only.

2. The competition for the medal shall be open to candidates whose age must not exceed thirty.

3. The candidates for the prize shall be required to submit an age certificate or corroboration of the same, confirmed by the Head of the department where they have worked.

4. The candidates, when communicating for publication in the Society's Journal, the paper intended for competition, must clearly make a statement to that effect.

5. The candidates for the medal shall submit their application not later than 31st October in every year, stating the title of their papers and the issue of the Journal in which they have been published.

6. No paper, which was submitted or has already been submitted for any other prizes or any examination, other than the M.A. or M.Sc. examination of the Indian Universities will be accepted for the present competition.

7. The merits of the papers shall be judged either by the Council of the Society or by the Board of Examiners, appointed by it, whose decision shall be considered final.

The Chemistry of Jute-lignin. Part III. Action of Nitric Acid on Lignin.

By Pulin Behari Sarkar.

The present investigation deals with the action of nitric acid on jute-lignin under varying conditions. Much work has been done in this line with other lignins with a view to elucidate their structure but different products have been obtained in different yields in each case. Oxalic acid (Rassow and Zickmann, *J. pr. Chem.*, 1929, **123**, 217; Hauser and co-workers, *Cellulosechem.*, 1921, **2**, 18) has been almost invariably obtained, whilst some have noticed melliotic acid (Fisher, Schrader and Frederick, *Ges. Ab. Kent. Hohle*, 1921, **6**, 1; Horn, *Bernstoff Chem.*, 1929, **10**, 364) and others nitro compounds (Powell and Whittaker, *J. Chem. Soc.*, 1924, **125**, 357). The production of oxalic acid in preponderent amount would point out to a carbohydrate structure as advanced by Willstätter and his colaborators (*Ber.*, 1922, **55**, 2637) whilst melliotic acid, although the question of drastic action in its formation is not precluded, would support the benzene structure of Schrauth (*Z. angew. Chem.*, 1925, **36**, 149). Jute-lignin gives oxalic acid (maximum yield, 38%) and a nitro product (yield varying from nil to 80%) under certain conditions. Oxalic acid has now been found among the oxidation products of catechol and protocatechuic acid which are degradation products of jute-lignin (*J. Indian Chem. Soc.*, 1933, **10**, 263). This observation, therefore, supports Freudenberg and his co-workers (*Ber.*, 1927, **60**, 581) in their view that lignin contains piperonylic acid residue. Table I gives the oxidation results and the production of oxalic acid under varying conditions. It is found that at the same temperature the greater the concentration of nitric acid, the greater is the amount of oxalic acid formed. Using the same strength of acid the yield increases with the temperature. Catalysts like vanadium pentoxide and ammonium vanadate diminish the yield.

Among the products of oxidation neither melliotic acid nor any sugar, as has been observed by Rasow and Linde (*Z. angew. Chem.*, 1931, **44**, 831), could be detected but acetic acid has been found, probably due to the oxidation of side chain. Contrary to the observation of Cross and Bevan ("*Cellulose*", 1918, p. 146), nitric acid in the presence of urea in excess has been found to have oxidising action on jute-lignin although to a less extent. Attempts to purify and identify the nitro product were not successful. It was not a homogeneous product, partly soluble and partly insoluble in water. It reduced Fehling's solution. Boiling with strong alkali did not give ammonia, neither could it affect the OCH_3 group showing that the latter is not in the form of an ester. Carboxyl group was found to be absent and the product could not be precipitated by carbon dioxide from alkaline solution. The nitro group could not be reduced and diazotisation failed after reduction. Neutral ammoniacal solution of the substance gave a silver salt. Table II gives the analyses of the nitro products obtained under varying conditions. It is found that the stronger the acid used, the lower is the methoxyl value and higher is the percentage of silver in silver salt; percentage of nitrogen and methoxyl vary inversely.

Experimental.

Preparation of jute-lignin.—Jute, previously boiled with 1% caustic potash for 1 hour, was treated with fuming hydrochloric acid for 6 hours. To the crumbled powder, thus obtained, 75% sulphuric acid was then slowly added with vigorous stirring and lignin was separated in the usual way after 10-12 hours.

Oxidation with nitric acid.—Oxidation was done with dilute as well as strong nitric acid. To dried and freshly prepared lignin (1g.) nitric acid (50 c. c)) was slowly added with occasional shaking. When strong acid was used the reaction mixture was cooled by ice. Reaction at 100° was done in a flask with an all glass reflux condenser. The mass was diluted with water, neutralised by ammonia and oxalic acid estimated as calcium oxalate. The acid obtained from the calcium salt had m. p. 101° and was identical with oxalic acid. Oxidation was also done in presence of catalysts like V_2O_5 and ammonium vanadate.

TABLE I.

Strength of nitric acid.	Temp.	Oxalic acid (anhydrous).	Time.	Residue.
Fuming	27°	24·3 g.	4 hrs.	2·10 g.
,,	100	38·1	2 hrs.	0·10
Strong (*d* 1·41)	2	23·67	4 days	4·6
,,	100	34·0	2 hrs.	0·16
5 *N*	29	21·0	4 days	16·9
,,	100	32·6	2 hrs.	1·26
2·5*N*	30	16·76	4 days	46·30
,,	100	29·0	4 hrs.	2·27
N	30	11·6	4 days	60·76
,,	100	21·0	4 hrs.	7·95
N/2	30	7·45	4 days	78·79
,,	100	17·62	4 hrs.	12·14
N/4	30	4·2	5 days	81·6
,,	100	15·52	4 hrs.	24·09

Action in the presence of urea.—(*a*) Lignin (1·25 g.), 2·5*N*-nitric acid (50 c. c.) and urea (10 g.) were heated for 4 hours at 100°. 1·25 G. of unchanged lignin was recovered.

(*b*) Lignin (1·35 g.) was added to a well cooled mixture of urea (5 g.) and strong nitric acid (*d* 1·41 ; 35 c. c.) and the mixture was well stirred and allowed to stand for 4 days at room temperature. 0·4450 G. of calcium oxalate was obtained corresponding to 1·996% oxalic acid.

Action of nitrous acid.—To a mixture of lignin (0·95 g.) and coarsely powdered sodium nitrite (70 g.) sufficient hydrochloric acid was added until effervescence ceased and the mixture was allowed to stand for 3 days ; 0·144 g. of oxalic acid corresponding to 15·2 % yield, was recovered from the reaction mixture.

Preparation of nitro product.—Lignin (10 g.) was treated with nitric acid (300 c.c.) with occasional stirring. The mixture, diluted with water, was filtered and the solid residue washed free from acid was redissolved in ammonia and filtered. The filtrate, when acidified

with hydrochloric acid, gave a deep brown substance which was dried at 110° and analysed. It was soluble in dilute alkalis and sodium carbonate solution but was insoluble in most organic solvents.

TABLE II.

Strength of nitric acid.	Solid.	Methoxyl.	Nitrogen (Kjeldahl).	Silver.	Hydroxyl.
Fuming	2·2%	8·27%	6·21%	26·12%	10·51%
Strong (d 1·41)	4·6	9·39	5·82	25·76	10·0
$5N$	16·9	9·82	5·82	24·83	9·82
$2·5N$	46·3	9·78	5·40	22·84	8·70
N (at 100°)	7·1	10·20	4·87	21·45	8·9
$0·5N$ (at 100°)	11·6	9·61	4·91	20·67	7·85

My grateful thanks are due to Professor Dr. J. K. Chowdhury for his kind and sympathetic encouragement during the course of the work and to Professor J. C. Ghosh for giving me every facility to carry it out.

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Received August 22, 1933.

Condensation of Pyruvic Acid with Aldehydes.

By Rajendra Nath Sen and Bijan Kumar Sen.

Claisen and Claparede (*Ber.*, 1882, **15**, 2472) first condensed pyruvic acid with benzaldehyde using dry hydrochloric acid gas as condensing agent and subsequently Erlenmeyer (*Ber.*, 1903, **36**, 2567; 1904, **37**, 1318) and Lubruzyuska and Smedley (*Biochem. J.*, 1913, **7**, 375) studied the condensation of pyruvic acid with different aldehydes, *e.g.*, benzaldehyde, cinnamic aldehyde, anisaldehyde and piperonal in presence of dilute caustic potash solution. The reaction proceeded in all cases at the laboratory temperature and the time required varied from 2 to 7 days and the yields varied from 50 to 70% of the theoretical.

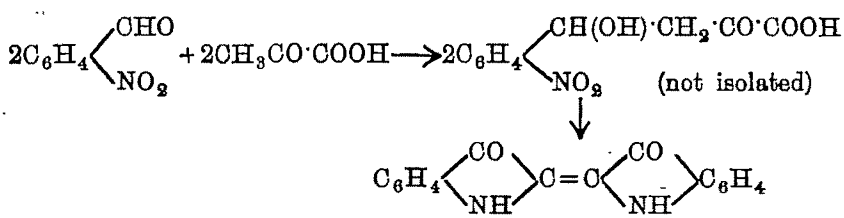
The object of the present work is to study further the condensation of pyruvic acid with benzaldehyde, substituted benzaldehydes and a few other aldehydes, aliphatic and heterocyclic, with a view to work out the optimum conditions under which the reaction may take place and also to see if the resulting α-keto-β-unsaturated acids can be converted into ring compounds on treatment with suitable dehydrating agents.

It has been found that a saturated solution of alcoholic caustic potash is the best condensing agent, which effects the condensation of benzaldehyde with pyruvic acid completely in 15—20 minutes at the ordinary temperature producing the potassium salt of the acid in good yield. The acid is identical in properties to the compound described by Claisen and Claperede (*loc. cit.*) and also by Erlenmeyer (*loc. cit.*). It gives a hydrazone and the presence of the ethylene linking is proved by the formation of a dibromo derivative. On heating the acid with acetic acid and fused sodium acetate at 180-90° ring formation takes place and the resulting product, decomposing at 115-20° and producing phthalic acid on oxidation, has been definitely identified with β-naphthaquinone.

The condensations of the nitrobenzaldehydes with pyruvic acid in presence of alcoholic potash have led to interesting results. The unsaturated acid from *p*-nitrobenzaldehyde is yellow,

A remarkable phenomenon has been noticed on heating the yellow acid to 160-65°, when it changes to a red variety, which has been found to have the same composition as the yellow variety, the two varieties differing also in their solubilities. The red variety is again transformed into the yellow variety on continued boiling with dilute alcohol. This may be a case of geometrical isomerism or chromo-isomerism (nitro and acinitro compounds).

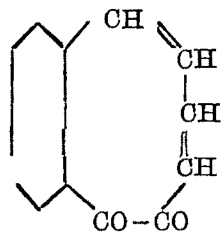
It has been further observed that the yellow compound, when heated to 175-80°, at first changes to the red variety and is then transformed into a ring compound which is insoluble in sodium bicarbonate and does not melt up to 230°. As the possibility of the ring formation is greater when the COOH group and the phenyl radical are on the same side, it appears that the red form corresponds to the *syn*-structure and the yellow form to the *anti*-structure. It has not been possible to isolate two isomers in the case of the acid derived from *m*-nitrobenzaldehyde, which is dull red. In this case ready ring formation does not take place. The condensation of *o*-nitrobenzaldehyde with pyruvic acid leads to the formation of 10% indigo and a small quantity of a dull red compound which has not been further investigated. Indigo is probably thus formed:



Cinnamic aldehyde, piperonal and anisaldehyde have been condensed with pyruvic acid and it has been generally found that the condensations readily take place with alcoholic caustic potash, while it requires several days for the completion of the reaction in the presence of hydrochloric acid.

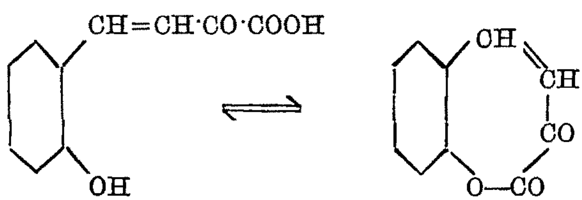
As previously noticed by Erlenmeyer (*loc. cit.*) and also by Labrazyuska and Smedley (*loc. cit.*) the unsaturated acids derived from cinnamic aldehyde, as well as piperonal, also exist in two isomeric forms; one variety readily changing to the other form. All these keto acids are converted into ring compounds by heating with acetic anhydride and fused sodium acetate; the acid from cinnamic aldehyde producing an eight-membered ring compound (*cf.* Sen and Roy, *J. Indian Chem. Soc.*, 1930, 7, 402) which is insoluble in sodium

carbonate but breaks on heating with dilute alkalis and also with water.



Furfural and citral have also easily been condensed with pyruvic acid in the presence of alcoholic caustic potash to produce the keto acids which yield hydrazones and bromo derivatives; but it has not been possible to obtain ring compounds from them.

The condensation of the hydroxybenzaldehydes, *e. g.*, *o*- and *p*-hydroxybenzaldehydes, β-resorcylaldehyde with pyruvic acid is an interesting study; while *p*-hydroxybenzaldehyde condenses in the presence of alcoholic potash as well as hydrochloric acid gas to form the keto-unsaturated acid, salicylaldehyde produces using either of the condensing agents a mixture of two compounds; one, a yellow crystalline substance decomposing at 185-90° and another, a red compound. It appears that the yellow product is the free hydroxy acid, while the red compund is the lactone, which is insoluble in

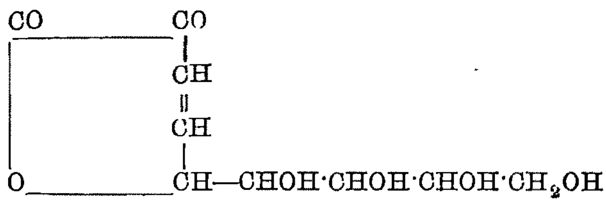


sodium carbonate but breaks and dissolves when kept in contact with water or with dilute caustic alkalis. The free acid, on boiling with strong hydrochloric acid, produces the lactone (red compound).

β-Resorcylaldehyde condenses with pyruvic acid at 220° using concentrated hydrochloric acid to produce a seven-membered lactone, which breaks up in contact with dilute alkalis. It is interesting to note that these seven-membered lactones from salicylaldehyde and β-resorcylaldehyde have dyeing properties like similar compounds from levulinic acid (*cf.* Sen and Roy, *loc. cit.*); the lactone from salicylaldehyde dyeing silk a yellowish-red shade while the lactone from

β-resorcylaldehyde dyes a deeper shade. Coumarin, a six-membered lactone, possesses neither colour nor any dyeing property. The dyeing property and colour of these lactones can only be attributed to their being seven-membered ones, with two CO groups.

Glucose has also been condensed with pyruvic acid in the presence of dry hydrochloric acid gas to form in 90% yield a deep red compound, which behaves like a lactone breaking up when kept in contact with dilute alkalis. This compound has probably got the following structure:



EXPERIMENTAL.

Cinnamylformic acid.—To a mixture of pyruvic acid (8·5 c. c.) and benzaldehyde (5·5 c. c.), alcoholic caustic potash (2·5 g. in 10 c. c. rectified spirit) was added drop by drop in the cold and the mixture shaken. The colour deepened and in 15 minutes the mixture solidified. The solid mass of potassium salt was purified from hot alcohol. (Found: K, 18·12. $C_{10}H_7O_3K$ requires K, 18·22 per cent). The free acid is a yellow thick liquid and was purified by washing with hot water and was then extracted with ether, the ethereal solution dried and the ether evaporated off in vacuum, yield 5 g. (Found: C, 67·67; H, 4·51. $C_{10}H_8O_3$ requires C, 68·19 ; H, 4·55 per cent).

The *dibromo derivative*, prepared by shaking the alcoholic solution of the acid with bromine water, crystallised from dilute alcohol as yellowish needles. (Found: Br, 47·71. $C_{10}H_8O_3Br_2$ requires Br, 47·61 per cent).

The *phenylhydrazone*, prepared in the usual manner, was obtained from dilute alcohol as an orange-red compound. (Found: N, 10·2. $C_{16}H_{14}O_2N_2$ requires N, 10·53 per cent).

The ring compound (β-naphthaquinone) was obained by heating the acid with acetic anhydride and fused sodium acetate at 180-90° for nearly 8 hours. The whole mass was then poured into a solution of sodium bicarbonate and left overnight. A red mass separated which was repeatedly washed with hot water and finally purified from rectified spirit. It decomposes at 115-20° and is identical with β-naphthaquinone in solubilities and in other properties,

The other compounds, prepared in a similar way, are described in the Table.

TABLE.

Aldehyde used and the derivatives of the product.	Formula.	Analysis Found.	Analysis Calc.	Remarks.
p-Nitrobenzaldehyde	$C_{10}H_7O_5N$	N, 6·07%	6·33%	Yellow crystals, readily soluble in acetic acid, alcohol, acetone; changes to red at 165°. Red variety transformed to yellow by boiling with alcohol and water.
— K salt.	$C_{10}H_6O_5NK$	K, 15·17	15·06.	Red.
— dibromo derivative	$C_{10}H_7O_5NBr_2$	Br, 41·58	42·00	Needles from alcohol, soften at 95°.
— phenylhydrazone	$C_{16}H_{13}O_4N_3$	N, 13·49	13·55	Needles from alcohol, m. p. 186°.
Ring compound	$C_{10}H_5O_4N$	N, 7·09	6·90	Prepared from the yellow acid by heating to 170-180°. Small needles from alcohol or acetone not melting up to 230°; also obtained by heating the acid with acetic anhydride.
m-Nitrobenzaldehyde.	$C_{10}H_7O_5N$	N, 6·21	6·33	Red, does not melt up to 260°. K salt very hygroscopic.
— dibromo derivative	$C_{10}H_7O_5NBr_2$	Br, 41·8	42·00	Yellow from dilute alcohol.
— phenylhydrazone	$C_{16}H_{13}O_4N_3$	N, 13·65	13·55	Red.
o-Nitrobenzaldehyde	$C_{16}H_{10}O_2N_2$	N, 10·74	10·69	Indigo.
Cinnamic aldehyde	$C_{12}H_{10}O_3$	C, 70·92	71·29	Orange-red, m. p, 74°, soluble in alcohol, acetic acid and acetone. If kept in a vacuum desiccator for some days the orange-red variety changes to yellow, m. p. 104-5°.
		H, 4·51	4·95	

Aldehyde used and derivatives of the product.	Formula.	Analysis Found.	Analysis Calc.	Remarks.
— K-salt	$C_{12}H_9O_3K$	K, 16·16%	16·25%	Yellow.
— phenylhydrazone	$C_{18}H_{16}O_2N_2$	N, 9·72	9·61	Red, m. p. 152°,
— dibromo derivative	$C_{12}H_{10}O_3Br_2$	Br, 44·63	44·22	Colourless, m. p. 114°.
— ring compound	$C_{12}H_8O_2$	C, 78·48 H, 4·82	78·2 4·82	Prepared by heating with acetic anhydride and sodium acetate at 200-10°. Red; m. p. 223° soluble in alcohol, acetone, acetic acid, unstable and dissolves in dilute alkali.
Piperonal	$C_{11}H_8O_5$	C, 59·56 H, 3·95	60·01 3·63	Yellow, changes colour at 70° and then melts at 162-63°. The yellow variety changes to a beautiful orange-red variety (m. p. 162-63°) in contact with HCl or heated to 70°.
— K-salt	$C_{11}H_7O_5K$	K, 14·96	15·12	
— dibromo derivative	$C_{11}H_8O_5Br_2$	Br, 42·42	42·10	M. p. 102°.
— phenylhydrazone	$C_{17}H_{14}O_4N_2$	N, 9·34;	9·03	Yellow, m. p. 174°.
— ring compound	$C_{11}H_6O_4$	C, 64·92 H, 3·22	65·34 2·97	Prepared by heating with acetic anhydride and sodium acetate at 200-10°, m. p. 160°.
Anisaldehyde	$C_{11}H_{10}O_4$	C, 63·95 H, 5·32	64·67 4·85	Yellow, soluble in alcohol, acetic acid, ether, chloroform, acetone and hot water.
— K-salt	$C_{11}H_9O_4K$	K, 15·74	15·99	
— dibromo derivative	$C_{11}H_{10}O_4Br_2$	Br, 44·17	43·71	Colourless, m. p. 82-85°.
— phenylhydrazone	$C_{17}H_{16}O_3N_2$	N, 9·49	9·46	Orange-red, m. p. 158°.
— ring compound	$C_{11}H_8O_3$	C, 70·08 H, 4·61	70·21 4·26	Prepared by heating with acetic anhydride and sodium acetate at 200°. Red, sparingly soluble in alcohol.

Aldehyde used and the derivatives of the product.	Formula.	Analysis. Found.	Calc.	Remarks.
Furfuraldehyde	$C_8H_8O_4$	C, 57·45%	57·84%	Yellow, m. p. 110°.
		H, 4·20	3·62	
— K-salt	$C_8H_5O_4K$	K, 19·36	19·12	Yellow.
— phenylhydrazone	$C_{14}H_{12}O_3N_2$	N, 10·98	10·94	Deep yellow, m. p. 162° (decomp.).
Citral	$C_{13}H_{18}O_3$	C, 70·06 H, 4·52	70·26 8·11	Reddish liquid of thick consistency, soluble in alcohol, acetic acid, acetone and ether.
— K-salt	$C_{13}H_{17}O_3K$	K, 15·36	15·00	The salt separates as a pasty mass which solidifies at 120°.
p-Hydroxybenzaldehyde	$C_{10}H_8O_4$	C, 62·17	62·5	Dry HCl is used as the condensing agent. Red liquid.
		H, 4·56	4·17	

Condensation of salicylaldehyde with pyruvic acid. (*i*) *With alcoholic potash.*—Pyruvic acid (3·5 c. c.)and salicylaldehyde (5 c. c.) were condensed in presence of caustic potash (2·5 g.) dissolved in alcohol (10 c. c.). On acidification two products were obtained: one is a yellow crystalline substance found to be the free acid while the other, a red compound, is the lactone of the acid.

(*ii*) *With* HCl.—The condensation was also effected by passing dry hydrochloric acid gas through a mixture of the two and leaving the whole thing for a week. On pouring the mixture into a little alcohol, the yellow free acid separated. It was purified by dissolving in caustic soda, the alkaline solution extracted with ether to remove unaltered aldehyde and then acidified. It was finally purified from alcohol or chloroform, yield 20%. It decomposes at 185-90°. (Found: C, 62·83 ; H, 4·61. $C_{10}H_8O_4$ requires C, 62·5 ; H, 4 17 per cent).

On diluting the alcoholic solution after removal of the yellow free acid, a red compound was obtained. It was purified by washing with chloroform to remove the free acid. It does not melt up to 285°. It is soluble in alcohol, ether, acetic acid, insoluble in benzene, carbon bisulphide and carbon tetrachloride. It is very unstable easily changing to yellow acid on boiling with alcohol, water or dilute alkali. It dyes silk a yellow shade. (Found: C, 68·77 ; H, 3·91 $C_{10}H_6O_3$ requires C, 68·98 ; H, 3·45 per cent).

Condensation of β-resorcylaldehyde with pyruvic acid.—A mixture of pyruvic acid (3·5 c. c.), β-resorcylaldehyde (5 g.), concentrated hydrochloric acid (20 c. c.), was heated at 200-20° for nearly 2 hours when a red compound separated. It was purified from acetic acid or alcohol. It dyes silk a red shade. (Found: C, 62·71 ; H. 3·90. $C_{10}H_7O_4$ requires C, 62·84 ; H, 3·67 per cent).

Condensation of glucose with pyruvic acid.—Dry hydrochloric acid gas was passed for nearly 2 hours through a solution of glucose (8 g.) and pyruvic acid (4 c. c.) in alcohol (20 c. c.) and the whole thing was kept for 5 days. On pouring the mixture into water a deep red compound was obtained. It was purified by precipitation from dilute alcohol. It does not melt up to 240°. (Found: C, 46·84 ; H, 5·42. $C_9H_{12}O_7$ requires C, 46·84 ; H, 5·17 per cent).

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Note on the Formation of a Ruby-red Jelly of Zirconium Sulphosalicylic Acid

BY SATYA PRAKASH AND LAXMI NARAIN BHARGAVA.

The preparation and properties of zirconium sulphosalicylic acid jellies have already been reported (*J. Indian Chem. Soc.*, 1933, **10**, 281). It was observed that when a concentrated solution of zirconium oxychloride is added to a strong solution of 5-sulphosalicylic acid, the mixture on standing for some hours sets to transparent or opalescent jellies. The authors have now observed that when zirconium sulphosalicylic acid jelly is allowed to set in presence of aluminium nitrate or nitric acid solution, it begins to develop a reddish tinge after a few hours and by the time of the setting of the jelly it assumes a very fine ruby-red colour. The colour of the jelly is preserved for months.

Different amounts of 50% sulphosalicylic acid (3·99*N*) were mixed with a solution of zirconium oxychloride, corresponding to 310·68 g. ZrO_2 per litre in presence of 0·914*N* aluminium nitrate solution and the following observations were made.

TABLE I

Total volume was made up to 5 c.c. by adding water. $ZrOCl_2$=1 c.c.

Sulphosalicylic acid.	Aluminium nitrate.	Observations.
2·0 c.c.	0 c.c.	White opalescent jelly in 16 hrs.
2·0	1·0	Slightly pink jelly in 19 hrs.
2·0	1·5	Pink jelly in 21 hrs. with opalescence.
2·5	0·0	White opalescent jelly in 21 hrs.
2·5	1·0	Transparent ruby-red jelly in 23 hrs.
2·5	1·5	Transparent ruby-red jelly in 24 hrs.

TABLE II.

Total volume = 5 c.c. $ZrOCl_2$ = 1 c.c.

Sulphosalicylic acid.	HNO_3 (1·09N).	Observations.
2·0 c.c.	0 c.c.	White opalescent jelly in 16 hrs.
2·0	1·0	Pink jelly in 40 hrs.
2·0	1·5	Red jelly in 40 hrs.
2·0	2·0	Ruby-red jelly in 50 hrs.
2·5	0	White opalescent jelly in 21 hrs.
2·5	1·0	Ruby-red jelly in 40 hrs.
2 5	1·5	Ruby-red jelly in 40 hrs.

The development of colour has also been studied by Nutting's spectrophotometer in the regions 5400Å and 6600 Å. For comparison, the results with the jelly to which no aluminium nitrate was added are also given. The jelly was prepared by mixing 3 c. c. of zirconium oxychloride and 4 c. c. of sulphosalicylic acid with 5 c. c. of water in the case of blank jelly and with 5 c.c. of 0·914N aluminium nitrate in the case of ruby-red jelly. Time of the setting of the jelly was 42 hours.

TABLE III.

Time.	Extinction coefficients			
	Colourless jelly.		Red jelly.	
Region⟶	5400 Å.	6600 Å.	5400 Å.	6600 Å.
0 day	0·10	0·06	0·08	0·04
1	0·11	0·19	0·10	0·04
2	0·11	0·18	0·33	0·15
3	0·16	0 15	0·52	0·15
4	0·23	0·16	0·80	0·17
8	0·25	0·15	1·33	0·17

The results of Table III show that during the course of 8 days, in the jelly to which no aluminium nitrate was added, the absorption in both the regions was almost of the same order, while in the presence of nitrate, the absorption in the red region, 6600 Å, is almost the same as in the case of colourless jelly but the opacity is much developed in the green region 5400 Å.

The colour of the jellies in the case of nitric acid becomes yellowish brown on keeping for a month, while in presence of aluminium nitrate, it remains as such. In presence of sodium nitrate, a jubiliant yellow coloured jelly is obtained.

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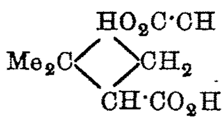
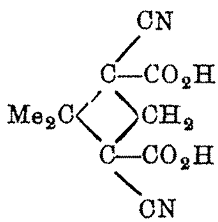
Two New Methods of Synthesis of Norpinic Acid.

BY K. N. GAIND AND P. C. GUHA.

A number of unsuccessful attempts (Ganguli, *J. Indian Inst. Sci.*, 1922, **5**, 23; Clemo and Welch, *J. Chem. Soc.*, 1928, 2621) have been made to achieve the synthesis of norpinic acid to which Bayer assigned the formula (I).



(I)

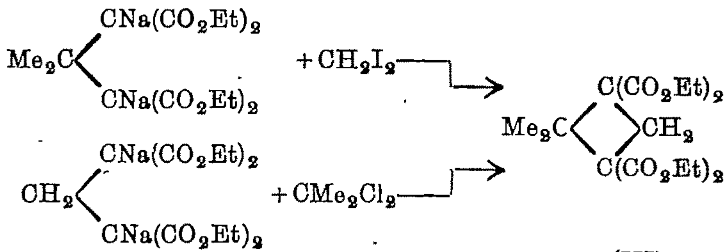


(II)

Kerr (*J. Amer. Chem. Soc.*, 1929, **51**, 614) has, however, finally succeeded in achieving this synthesis by the condensation of the sodium derivative of Gaureschi imide with methylene iodide, and by hydrolysing the bridged imide thus formed into the cyano acid (II) and finally into *trans*-norpinic acid (I). Shoppee and Simonsen (*J. Soc. Chem. Ind.*, 1929, **48**, 730) converted this into *cis*-norpinic anhydride and the *cis*-acid, and established its identity with the acid obtained from *dl*-pinonic acid. As Kerr's method is round about and when repeated in this laboratory was found not to give the yield described by the author, it seemed desirable to try the synthesis of this acid by the condensation of sodium methylenedimalonic ester and $\beta\beta$-dichloropropane. It is to be mentioned here that though this scheme is not much different from the unsuccessful scheme of Clemo and Welch (*loc. cit.*), the success achieved in these experiments is primarily due to the application of a convenient method* discovered by one of us (P. C. G.), *viz.*, of bringing about the condensation of alkylenedihalides with suitable disodium

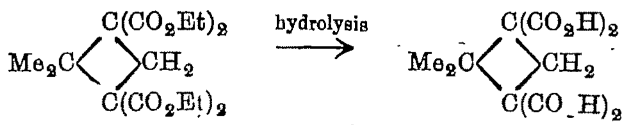
* This method has already been found to be of general applicability and has been adopted for the synthesis of ethyl ketoapopinane dicarboxylate by the action of trimethylene bromide upon the disodium derivative of ketonorpinic ester, also in bridging succinosuccinic ester *via* its disodium derivative by means of methylene iodide, etc. (*cf. Current Science*, 1933, **2**, 53).

derivative of compounds in benzene suspension by prolonged heating in a sealed vessel at a high temperature, thus leading to the formation of ring-closed compounds. The tetracarboxylic ester (III),

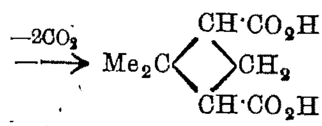


(III)

obtained by the action of methylene iodide and $\beta\beta$-dichloropropane respectively upon the disodium derivatives of *iso*propylidenedimalonic ester and methylenedimalonic ester has yielded norpinic acid on hydrolysis and decarboxylation according to the following scheme:



(IV)



(I)

As the result of a large number of experiments conducted under varying conditions it has been possible to effect considerable improvement upon the method of preparation of *iso*propylidenemalonic and dimalonic esters described by Clemo and Welch.

Experimental.

Preparation of iso*propylidenemalonic ester*.—A mixture of ethyl malonate (1170 g.), acetic anhydride (1080 g.) and a solution of anhydrous zinc chloride (90 g.) in acetone (990 g.) was heated in three round-bottomed flasks under reflux over free flames, so adjusted that the mixture did not boil very vigorously in the beginning. All possible precautions were taken to avoid contact with moisture. The

reaction mixture after 100 hours' continuous heating was poured into an equal volume of water, thoroughly shaken and then allowed to stand for 24 hours during which the unchanged acetic anhydride was converted into acetic acid. The ester layer was then separated and thoroughly washed with water. The ether extract of the aqueous washings was mixed with the ester and washed with sodium carbonate solution. After drying over anhydrous magnesium sulphate and removal of ether, the residue was repeatedly fractionated and the portion distilling at 116-120°/14 mm. collected, yield 1315 g. Clemo and Welch obtained 810 g. from 1170 g. of malonic ester.

Preparation of iso*propylidenedimalonic ester.*—*iso*Propylidenemalonic ester (80 g.) was heated in an autoclave in mixture of absolute alcohol and anhydrous benzene (1:1) with an equivalent of sodiomalonic ester for 48 hours at 160° at 100 lbs. pressure. The solid residue obtained after the removal of alcohol and benzene was dissolved in the minimum quantity of cold water, acidified with dilute sulphuric acid in the cold and the separated oil extracted with ether, dried over anhydrous magnesium sulphate, ether removed and the residual oily product repeatedly fractionated. The portion distilling at 170-172°/3 mm. was collected, yield 42 g. It was identified to be *iso*propylidenedimalonic ester by hydrolysis to $\beta\beta$-dimethylglutaric acid.

Action of $\beta\beta$-dichloropropane upon the sodium derivative of methylenedimalonic ester. Isolation of 2:2-*dimethyl*cyclo*butane*-1:1:3:3-*tetracarboxylic acid.*—Methylenedimalonic ester (44 g.), prepared according to the method of Knoevenagel (*Ber.*, 1894, **27**, 2346) and thoroughly purified by repeated fractional distillation, was converted into its sodium derivative by heating under reflux with sodium (5 g.) in anhydrous benzene suspension for 8 hours. Most of the benzene was removed in *vacuo* and the residual jelly like mass heated with $\beta\beta$-dichloropropane (15 g) in a closed soda-water bottle for 30 hours in an oil-bath at 140° when sodium iodide settled at the bottom and the liquid appeared brown in colour and was quite mobile. To remove any unreacted methylenedimalonic ester, the reaction mixture was heated under reflux with sodium wire. The filtered solution was freed from benzene and the viscous brown oil subjected to fractional distillation at 4 mm. pressure; about half of the liquid distilled up to 180°. The residual liquid did not distil but showed signs of decomposition on further heating; so the distillation was discontinued at this stage. The contents of the distilling flask (about

10 g.) were kept for hydrolysis with potassium hydroxide (14 g.) in aqueous alcohol (100 c.c.) for 3 days. After removing the alcohol in *vacuo* the residual brown solid was dissolved in cold water and shaken repeatedly with ether. The alkaline solution was then carefully acidified with dilute hydrochloric acid under cooling and extracted with ether repeatedly. The yellow ethereal extract was dried over anhydrous magnesium sulphate, ether removed, and the light brown viscous residue kept in a vacuum desiccator when after about a fortnight it solidified. This was crystallised from acetone-benzene mixture being very soluble in the former, m.p. 200°. (Found: C, 45·8; H, 4·9. $C_{10}H_{12}O_8$ requires C, 46·1; H, 4·6 per cent).

Isolation of norpinic acid.—The above tetracarboxylic acid was heated in a liquid paraffin-bath to 220-240° till there was no more evolution of carbon dioxide (tested with lime water). The product was dissolved in water and the solution evaporated to dryness. The thick viscous mass thus obtained was kept in a vacuum desiccator, when it solidified after 24 hours, m.p. 144-45°. The solid was dissolved in water, filtered, concentrated to small bulk on a water-bath and allowed to stand in an ice chamber, when crystals, m.p. 146° (softening at 137°), separated after a week. No rise in the melting point was observed on further two recrystallisations; yield is very poor. (Found: C, 55·62; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 6·9 per cent).

The decarboxylation was also carried out by heating the tetra-acid under reflux with 50% sulphuric acid for 24 hours when the evolution of carbon dioxide ceased. After addition of water the mass was heated again and filtered. The filtrate was extracted repeatedly with ether. The residue left after removal of ether was purified as above.

Action of methylene iodide upon sodium derivative of iso*propylidenedimalonic ester.*—The sodium derivative of *iso*propylidenedimalonic ester, prepared by heating the ester (32 g.) with sodium wire (4·6 g.) in anhydrous benzene solution, was heated with methylene iodide (27 g.) in an oil-bath at 140° for 48 hours in a closed soda-water bottle. The neutral reaction product was worked up in the usual manner and 2:2-dimethyl*cyclo*butane-1:1:3:3-tetracarboxylic acid and norpinic acid were isolated and purified by following the method described in the foregoing experiment (the tetracarboxylic acid, m.p. 199°). (Found: C, 46·0; H, 4·8. $C_{10}H_{12}O_8$ requires C, 46·1; H, 4·6 per cent), and norpinic acid, m.p. 145-46° (softening at 136°).

(Found: C, 56·1; H, 7·2. $C_8H_{12}O_4$ requires C, 55·8; H, 6·9 per cent).

The melting point of the norpinic acid and the tetracarboxylic acid prepared as above remained undepressed on admixture with the corresponding samples prepared according to the method of Kerr (*loc. cit.*).

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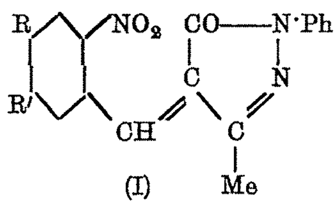
Quinoline Derivatives. Part II. Pyrazolinoquinolines.

By Kartar Singh Narang, Jnanendra Nath Rây and Anirudh Singh.

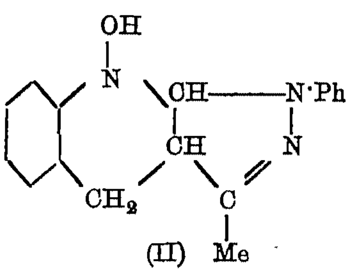
In the present investigation an attempt has been made to fuse a pyrazole ring system in the 2:3-position of a quinoline for obvious pharmacological reasons.

Aromatic *o*-nitroaldehydes condense with phenylmethylpyrazolones in presence of sodium acetate to give condensation products of the type (I).

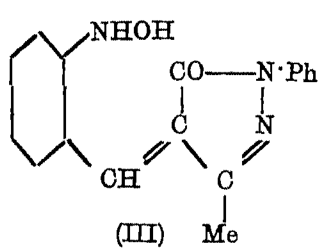


(I)

On reduction these substances do not smoothly pass to the corresponding quinolines. The product from *o*-nitrobenzaldehyde (I, R=R′=H) gives a tetrahydroquinoline (II).



(II)

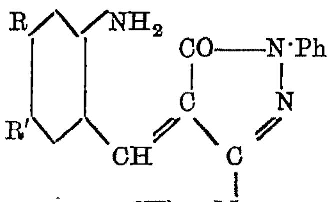


(III)

The reduction of the nitro compound obviously proceeds through a hydroxylamino compound (III) because from the mixed hydrochlorides of the crude reduction product the substance (III) can be isolated. McClusky (*J. Amer. Chem. Soc.*, 1922, **44**, 1575) has reported the formation of a similar quinoline oxide in the reduction of ethyl *o*-nitrobenzoylacetoacetate.

The substance (I) dissolves in acids and also in alkalis, a behaviour in keeping with its structure and gives a monohydrochloride with hydrochloric acid whilst a pyrazolinoquinoline is expected to form a dihydrochloride. The same substance is obtained if the reduction is carried with either aluminium amalgam or zinc dust and acetic acid or alcoholic hydrochloric acid.

The condensation product with nitropiperonal or nitroveratric aldehyde on reduction is converted to the related amine (IV), which



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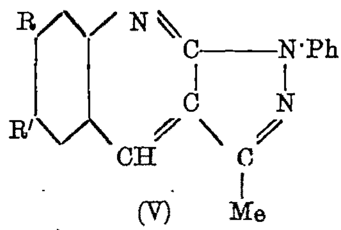


(V)

can be cyclised to the pyrazolinoquinoline (V) by heating with anhydrous sodium acetate in a current of hydrogen. It is noteworthy that whatever reducing agents are employed the substance (IV) is produced in every case and no simultaneous ring formation occurs (*cf.* Armit and Robinson, *J. Chem. Soc.*, 1922, **121**, 827, *et seq.*, who found that an *ortho*amino unsaturated ketone cyclises to a quinoline in presence of acetic acid but not in presence of hydrochloric acid). Therefore, it seems that the amino group is in *trans* position with respect to the ketonic grouping.

The substance gives a *trihydrochloride* which may be due to the addition of a molecule of hydrogen chloride at the double bond. Even the nitro compound which is of a striking colour becomes nearly colourless in presence of hydrochloric acid due no doubt to the destruction of conjugation owing to the addition of hydrogen chloride at the double bond.

The respective structures assigned to the compounds have been tested by means of their absorption spectra which confirmed the conclusions drawn.

EXPERIMENTAL.

o-*Nitrobenzylidine-1-phenyl-3-methylpyrazolone.*—An intimate mixture of phenylmethylpyrazolone (8·5 g.), *o*-nitrobenzaldehyde (8·0 g.) and freshly fused sodium acetate (3·5 g.) was heated to 150° for 2 hours with stirring. The pasty mass soon solidified and assumed

a dark red colour. It was washed with water and crystallised from alcohol in bright red needles, m.p. 162°, yield 8 g. (Found: N, 13·5. $C_{17}H_{13}O_3N_3$ requires N, 13·68 per cent).

Reduction wiih zinc dust and acetic acid.—(*a*) The nitro compouud (1 g.) was dissolved in acetic acid (20 c.c.) by heat and the solution was reduced with zinc dust in small quantities till the dark red solution turned pale yellow. The hot solution was filtered, hydrochloric acid (*d* 1·16, 2 c.c.) added and diluted to 100 c.c. with water and the solution saturated with ammonium chloride, when a pale yellow subtance (0·6 g.) crystallised out. It was crystallised from hot methanol containing hydrochloric acid, m.p. 251-52°. [Found: N*, 13 1 ; Cl, 11·2 (by precipitation with silver nitrate in alcoholic solution). $C_{17}H_{17}ON_3$, HCl requires N, 13·3 ; Cl, 11·3 per cent].

(*b*) The nitro compound (0·5 g.) dissolved in moist ether (100 c.c.) was reduced with aluminium amalgam during 24 hours, when the dark red solution became pale pink. Removal of the solvent furnished a substance which had m.p. 252° after crystallisation from methyl alcohol and hydrochloric acid and showed no depression on admixture with the product described under (*a*).

(*c*) The nitro compound (0·5 g.) dissolved in alcohol (20 c.c.) was reduced with zinc dust and hydrochloric acid and after the removal of the solvent the product was worked up as under (*a*) when the same substance as described under (*a*) and (*b*) was obtained.

Isolation of the base (II).—The crude hydrochloride obtained in the reduction of the nitro compound with zinc dust (1 g.) suspended in water (50 c.c.) was treated with ammonia (*d* 0·8, 10 c.c.) when a clear solution resulted. On concentration of the solution in *vacuo* at 60° a colourless substance (A) (0·8 g.) crystallised out and from the filtrate chloroform extracted a dark coloured pasty substance (B). The substance (A) was crystallised from a mixture of benzene-ligroin in glistening needles, m.p. 142°. (Found: C, 72·7 ; H, 6·4 ; N, 15·1. $C_{17}H_{17}ON_3$ requires C, 72·8 ; H, 6·1 ; N, 15·1 per cent).

The dark coloured pasty substance (B) was triturated with petroleum ether and a brown coloured solid was obtained. It crystallised from hot benzene (charcoal) in colourless needles, m.p. 101-102°. (Found: N*, 14·4. $C_{17}H_{15}O_2N_3$ requires N, 14·3 per cent). It is probably the substance (III), since it reduced ammoniacal silver nitrate instantaneously and after heating with acids gave the test for a diazotisable amine.

Condensation of nitropiperonal with phenylmethylpyrazolone.—A mixture of nitropiperonal (4 g.), phenylmethylpyrazolone (3·6 g.) and fused sodium acetate (3 g.) was heated at 185° for 2 hours. The product after treatment with water was well washed with boiling alcohol and crystallised from hot acetic acid in red silky needles, m.p. 199°, yield 4 g. (Found: N*, 11·9. $C_{18}H_{13}O_5N_3$ requires N, 12·0 per cent). The nitro compound (1 g.), dissolved in hot acetic acid (30 c.c.), was treated with small quantities of zinc dust in such a manner as to keep the solution boiling gently till the solution became pale yellow. It was filtered and treated with hydrochloric acid (*d* 1·16), diluted with water to 80 c.c. and treated with ammonium chloride when a pale yellow substance (0·6 g.) separated. Crystallised from methyl alcohol-hydrochloric acid it came out as delicate colourless needles, m.p. 248°. Reduction of the nitro compound with aluminium amalgam also furnished the same product. (Found: N*, 9·8; Cl, 24·0. $C_{18}H_{15}O_3N_3$, 3 HCl requires N, 9·8; Cl, 24·7 per cent). The substance showed the presence of a diazotisable amino group.

The *hydrochloride* (1 g.) in water (100 c.c.) was treated with ammonia till it dissolved completely. The solution was concentrated in *vacuo* at 50° when a colourless crystalline substance separated which darkens in contact with air. It crystallised from hot alcohol in stout needles, m.p. 186°. (Found: C, 67·1; H, 5·3; N*, 13·1. $C_{18}H_{15}O_3N_3$ requires C, 67·3; H, 4·7; N, 13·1 per cent).

The *base* (1 g.) was well mixed with fused sodium acetate (3 g.) and was heated in a current of dry hydrogen at 186° for a few minutes and then at 150° for 1 hour. The product, well washed with water, was crystallised from hot alcohol (charcoal) in pale yellowish needles, m.p. 185°, mixed m.p. with the amine 155-170°, yield 0·02 g. (Found: C, 71·2; H, 4·5; N*, 13·71, 13·92. $C_{18}H_{13}O_2N_3$ requires C, 71·3; H, 4·3; N, 13·86 per cent). The substance does not show the presence of an amino group and gives a picrate.

The product of the condensation of nitroveratric aldehyde and phenylmethylpyrazolone conducted at 145° was isolated as in the previous cases. It crystallised from hot dilute acetic acid in brilliant red silky needles, m.p. 183°. (Found: N*, 11·1. $C_{19}H_{17}O_5N_3$ requires N, 11·4 per cent).

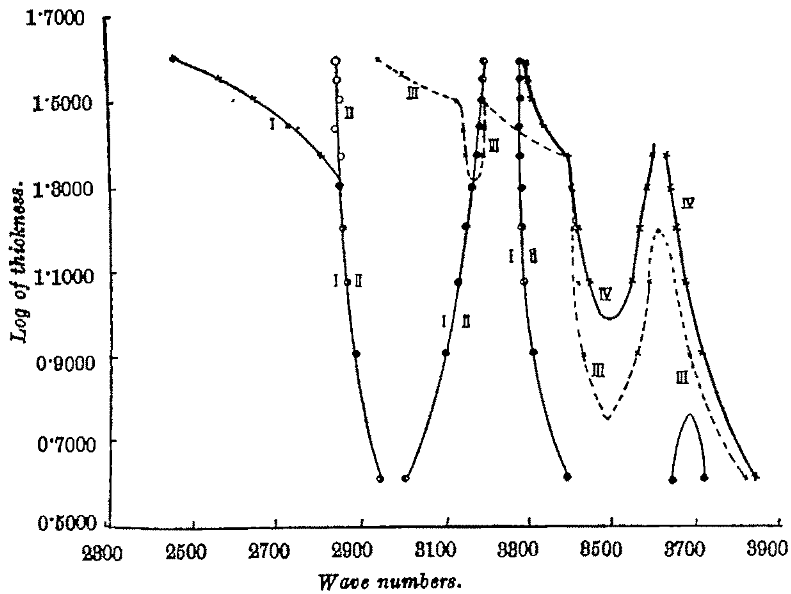
The nitro compound (4 g.) dissolved in hot acetic acid (100 c.c.) was reduced with zinc dust till the solution became pale yellow. The filtered solution was concentrated to 20 c.c. in *vacuo* and then diluted with water and a few drops of concentrated hydrochloric acid.

On saturation with ammonium chloride, the hydrochloride crystallised, which was recrystallised from amyl alcoholic hydrochloric acid in colourless needles, m.p. 226°, yield 2·3 g. [Found: N*, 9·5, 9·6; Cl, 23·2 (by precipitation). $C_{19}H_{19}O_3N_3$, 3HCl requires N, 9·4; Cl, 23·8 per cent].

The grey coloured base (1 g.), isolated as in the previous case, did not give a sharp m.p. even after repeated crystallisations from benzene and other solvents, indicating that partial cyclisation had occurred. The crude base was mixed with sodium acetate and heated at 150° for $1\frac{1}{2}$ hours. The product after treatment with water crystallised from alcohol (charcoal) in pale yellow needles, m.p. 215°, yield 0·05 g. (Found: N*, 13·2. $C_{19}H_{17}O_2N_3$ requires N, 13·2 per cent).

The absorption spectra of the quinolines (V, R=R′=OMe, and R=R′=O_2CH_2) numbered as I and II respectively in the curve, that of IV (numbered as III) and that of I (numbered as IV) were taken in a concentration $M/10000$ in chloroform. The spectroscopic results show that the curves I and II are similar in character whilst IV differs markedly from both I and II. The curve III of the amino compound is again different from I, II and IV.

FIG. 1



* Analyses marked ' * ' were done by the micro method.

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Received February 26, 1934.

Rotatory Powers of Some Disubstituted Camphoranilic Acids.

By Mahan Singh and Bikram Singh.

The work on disubstituted camphoranilic acids (*J. Chem. Soc.*, 1931, 478; *J. Indian Chem. Soc.*, 1932, 9, 363) has been further extended to include methyl chlorocamphoranilic acids.

The rotatory powers of 2′-methyl-5′-chloro-, 2′-methyl-4′-chloro-, 2′-methyl-3′-chloro-, 4′-methyl-2′-chloro- and 2′-methoxy-4′-chlorocamphoranilic acids have been determined in four solvents, methyl alcohol, ethyl alcohol, acetone and methyl ethyl ketone for two wave-lengths, Hg_{5780} and Hg_{5461}. The mercury violet is rather dim and, therefore, the rotatory powers could not be measured in all the cases.

The following tables record the molecular rotatory powers of methylchlorocamphoranilic acids, methylcamphoranilic acids and chlorocamphoranilic acids.

Table I.

$(M)_{Hg_{5780}}$

	2′-Methyl 5′-chloro-.	2′-Methyl- 4′-chloro-.	2′-Methyl- 3′-chloro-.	4′-Methyl- 2′-chloro-.
MeOH	211·8	174·7	145·5	76·3
EtOH	210·3	165·0	142·3	56·6
Me_2CO	132·5	124·6	66·2	Almost nil
MeEtCO	166·6	129·4	89·0	10·1

Table II.

$(M)_{Hg_{5780}}$

	o-Me.	*m*-Me.	*p*-Me.	*o*-Cl.	*m*-Cl.	*p*-Cl
MeOH	144·5	137·3	162·6	54·1	147·0	166·3
EtOH	127·2	121·3	137·3	30·9	119·2	142·3
Me_2CO	83·1	93·9	98·2	−21·4	100·5	126·9
MeEtCO	104·7	108·3	137·3	−10·2	131·5	148·6

It will be seen from the study of the tables that the introduction of a chlorine atom in the first three cases leads to the enhancement of rotation, the maximum effect being when the methyl and the chlorine, both of similar polarity, are in the *para* position with respect to one another. The effect is the least when the two groups are present in the *ortho* position with respect to one another. In the 4th compound the chlorine atom is present in the *ortho* position with respect to the substituted-amino group. There is a very great fall in the rotation of the original compound; in methyl alcohol from 162° to 76° and in ethyl alcohol from 187·3° to 56·6°. This fall in the rotatory power is very marked in the ketonic solvents; in acetone the fall is from 98·0° to almost zero, and in methyl ethyl ketone from 137° to 10°. 2′-Chloro-4′-methylcamphoranilic acid was examined in acetone in a very concentrated solution and the difference between the solvent and the solution readings were so small as to be within the experimental error. It has been shown by Singh and Singh in the case of *o*-chlorocamphoranilic acid (*J. Chem. Soc.*, 1927, 1994. *cf.* also experimental), and by Forster and Spinner (*J. Chem. Soc.*, 1919, **115**, 889), in the case of *o*-chlorophenyliminocamphor that chlorine in the *ortho* position has a great depressing effect on the rotatory power of the original compound.

The question may be looked at from the point of view of the introduction of the methyl group. In the first three cases the methyl group enters into the *ortho* position with respect to the substituted amino group, so that it is in close proximity to the optically active group. It is, therefore, reasonable to suppose that it will exert a uniform influence on the chlorocamphoranilic acids. It increases the rotatory power considerably when it goes into the *para* position with respect to the chlorine atom. It has very little effect when it is in the *meta* position with respect to the chlorine, but when present in the *ortho* position with regard to the chlorine atom, it has some depressing influence in the ketonic solvents.

In the 4th compound the methyl group is present in the 4′-position and it has raised the rotations of 2′-chlorocamphoranilic acid to a small extent.

A methoxy group in the 2′-position is also known to have a depressing effect (Singh and Singh, *J. Chem. Soc.*; 1930, 1301; *cf.* also Rule and others, *ibid.*, 1928, 1498), In 2′-methoxy-4′-chlorocamphoranilic acid the rotatory powers are lower than those of the 4′-chlorocamphoranilic acid in all the solvents examined.

Influence of the solvent on the rotatory power.—The solvents employed in the decreasing order of their dielectric constants are methyl alcohol, ethyl alcohol, acetone, ethyl methyl ketone. A reference to the tables will show that the sequences of solvents in order of decreasing or increasing rotatory power is the same as their dielectric constants except that the position of ethyl methyl ketone and acetone is reversed. But this regularity does not extend to 3′-chlorocamphoranilic acids and 4′-chlorocamphoranilic acid, where the sequence of ethyl methyl ketone and ethyl alcohol is also reversed.

EXPERIMENTAL.

Condensation of camphoric anhydride with chlorotoluidines and chloroanisidine.—Camphoric anhydride and the amine (equimol.) were heated together with fused sodium acetate at 140—50° for 3-4 hours. The product was dissolved in alcohol and precipitated with water, when a brown mass came down. It was extracted with a dilute solution of caustic soda or ammonia to remove any imide. The filtered solution was then acidified with dilute hydrochloric acid. The white solid thus obtained was recrystallised from alcohol (charcoal).

2′-Methyl-5′-chlorocamphoranilic acid crystallised from alcohol in needles, m.p. 206°. It is soluble in the usual organic solvents. (Found: N, 4·5; Equiv., 322·5. $C_{17}H_{22}O_3NCl$ requires N, 4·3 per cent. Equiv., 322·5).

2′-Methyl-4′-chlorocamphoranilic acid crystallised from alcohol in silky needles, m.p. 221-22°. It is readily soluble in acetone and benzene and less readily in methyl alcohol and ethyl alcohol. (Found: N, 4·5; Equiv., 323. $C_{17}H_{22}O_3NCl$ requires N, 4·3 per cent. Equiv. 323·5).

2′-Methyl-3′-chlorocamphoranilic acid separated from alcohol in a crystalline mass, m.p. 219°. The quantity of the imide formed is appreciable in this case but no attempt was made to purify and analyse the compound. (Found: N, 4·50; Equiv., 325. $C_{17}H_{22}O_3$-NCl requires N, 4·3 per cent. Equiv., 323·5).

4′-Methyl-2′-chlorocamphoranilic acid crystallised from alcohol in needles, m.p. 206-07°. The yield of the acid is not so good as in the first three cases. The acid is readily soluble in ketone, less readily in alcohols. (Found: N, 4·65; Equiv., 323. $C_{17}H_{22}O_3NCl$ requires N, 4·3 per cent. Equiv., 323·5).

2-*Methoxy-5-chlorocamphoranilic acid* was obtained as a micro-crystalline mass, m.p. 176-77°, yield about 10%. It is soluble in the usual organic solvents. (Found: N, 4·3; Equiv., 339·5. $C_{17}H_{22}O_4NCl$ requires N, 4·12 per cent. Equiv., 339·5).

2′-, 3′- and 4′-Methylcamphoranilic acids and 2′-, 3′-, 4′-chlorocamphoranilic acids were prepared by the general method given above. The rotatory powers of these compounds have been determined for sodium light by Singh and Puri (*J. Chem. Soc.*, 1926, 504) and Singh and Singh (*loc. cit.*). The rotatory powers of these compounds have now been determined for two wave-lengths, namely Hg_{5780} and Hg_{5461}.

TABLE III.

Solvent.	Conc. (g./25 c.c.).	Hg_{5780} α.	Hg_{5461} α.	Hg_{4358} α.
		2′-Methyl-5′-chlorocamphoranilic acid.		
MeOH	0·2500	65·5	75·5	...
EtOH		65·0	74·5	112·5
Me_2CO		41·0	50·5	97·5
MeCOEt		51·5	63·0	...
		2′-Methyl-4′-chlorocamphoranilic acid.		
MeOH	0·2500	54·0	63·0	105·0
EtOH		51·0	59·0	103·0
Me_2CO		38·5	45·5	...
MeCOEt	0·2000	40·0	47·0	...
		2′-Methyl-3′-chlorocamphoranilic acid.		
MeOH	0·2500	45·0	52·5	96·5
EtOH		44·0	51·0	91·0
Me_2CO		20·5	30·5	...
MeCOEt	0·2000	27·5	40·0	...
		4′-Methyl-2′-chlorocamphoranilic acid.		
MeOH	0·2500	23·5	32·5	36·0
EtOH	,,	17·5	24·5	35·0
Me_2CO	0·4000	...	...	...
MeCOEt	,,	3·3	4·4	...

Solvent.	Conc. (g./25 c.c.).	Hg_{5780} α.	Hg_{5461} α.	Hg_{4358} α.
2′-Methoxy-5′-chlorocamphoranilic acid.				
MeOH	0·2500	38·0	45·0	...
EtOH	„	30·0	36·0	57·5
Me_2CO	0·3000	18·0	22·0	...
MeCOEt	„	19·37	23·79	...

TABLE IV.

	Hg_{5780} α.	Hg_{5461} α.	Hg_{5780} α.	Hg_{5461} α.	Hg_{4358} α.
	2′-Methylcamphoranilic acid. Conc. = 0·2000 (g./25 c.c.).		*2′-Chlorocamphoranilic acid.* Conc. = 0·3000 (g./25 c.c.).		
MeOH	50·0	65·0	17·5	21·0	350·
EtOH	44·0	55·0	10·0	12·0	17·5
Me_2CO	28·75	36·6	−6·9	−8·3	...
MeCOEt	36·25	45·8	−3·3	−4·0	...
	3′-Methylcamphoranilic acid. Conc. = 0·2000 (g./25 c.c.).		*3′-Chlorocamphoranilic acid.* Conc. = 0·2500 (g./25 c.c.).		
MeOH	47·5	62·5	47·5	62·5	...
EtOH	42·0	54·0	38·5	48·0	85·0
MeCO	32·5	42·4	32·5	40·0	...
MeCOEt	37·5	48·3	42·5	52·5	...
	4′-Methylcamphoranilic acid. Conc. = 0·2000 (g./25 c.c.).		*4′-Chlorocamphoranilic acid.* Conc. = 0·2500 (g./25 c.c.).		
MeOH	56·25	70·0	53·75	71·75	158·5
EtOH	47·5	57·5	46·0	59·0	105·0
MeCO	34·0	42·0	41·0	51·5	...
MeCOEt	47·5	57·5	48·0	62·5	...

The rotatory powers were determined in a 2-dcm. tube.

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Adsórption of Acids by Animal Charcoal.

By Saul Caspe.

Adsorption of acids by animal charcoal has long been accepted by chemists, and recently several mechanisms have been suggested as explanations of this phenomenon. The following experiment helps to demonstrate the mechanism of the so-called acid adsorption by animal charcoal.

Experimtal.

2 G. of animal charcoal (65% ash) were shaken with 100 c.c. of approximately $N/20$-acetic acid for 20 minutes. Another 2 g. of the same charcoal were shaken with 100 c.c. of approximately $N/20$-HCl for 20 minutes. The solutions were then centrifuged from the charcoal which settled out. The supernatant liquid and the stock solution of $N/20$-acetic acid were titrated for acidity; the supernatant liquid and the stock solution of $N/20$-HCl were titrated for acidity and chlorine content. All quantities of the acid solutions were pipetted out. The chlorine was determined by the Whitehorn modification of the Volhard method (Whitehorn, *J. Biol. Chem.*, 1921, 45, 449).

Reduction in acidity.

Solutions.	Quantity of soln.		Titre (average).
Stock soln.	20 c.c. $N/20$ (approx.) acetic acid		10·60 c.c. $N/10$-NaOH
,, ,,	,, $N/20$-HCl		11·36 ,, $N/10$-NaOH
Centrifuged soln.	,, ,,	-acetic acid	6·09 ,, ,, ,,
,, ,,	,, ,,	-HCl	6·44 ,, ,, ,,

The centrifuged solutions gave a strong qualitative test for phosphates.

Non-reduction in chlorine concentration.

Solution.	Quantity of soln.	Titre (average).
Stock soln.	2 c.c. ($N/20$) (approx.) HCl	6·60 c.c. $AgNO_3$
Centrifuged soln.	,, ,, ,, ,,	6·65 c.c. ,,

HCl factor = 1·136 $N/20$; $AgNO_3$ solution contains 0·002905 g./c.c. $AgNO_3$.

5

Animal charcoal acts similarly upon $N/20$-HCl and acetic acids: the reduction of hydrogen concentrations is approximately the same for both acids. Animal charcoal does *not* reduce the chlorine content of HCl. It, therefore, does not adsorb HCl but reacts with it in a manner described previously (*J. Chem. Ed.*, 1932, 9, 907); the phosphate impurities of this charcoal are converted to phosphoric acid by the action with HCl, and thus, a partially untitratable hydrogen results. The chlorine anion remains quantitatively unaffected by this reaction.

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The Photosynthesis of Nicotine.

By H. E. Watson and B. K. Vaidya.

In a recent communication (*J. Indian Chem. Soc.*, 1933, **10**, 453) Bhargava and Dhar claim to have obtained "practically pure nicotine hydrochloride" by exposing 2% formaldehyde solution containing ammonia to sunlight or to the light from a mercury arc. Quantities of ammonia varying from 40 to 12·5 c.c. of 6·2 N solution per litre were employed in presence of different catalysts. In all cases nicotine was obtained, and cupric carbonate appeared to be the best catalyst, but in the absence of any quantitative data, it is not clear upon what evidence this statement is based.

In order to separate the nicotine, the alkaline solutions were distilled and the nicotine extracted with ether from the *residue*. Since nicotine is readily volatile with steam it appears improbable that it would be obtained by this procedure even if it were formed. The authors also mention a method of separating hexamethylenetetramine and nicotine by forming the mercuric chloride compound. This appears unnecessary since the former substance is practically insoluble in ether while nicotine is readily soluble.

On examining the data from which the molecular weight was determined, apart from the difficulty of understanding how a value of 158·68 can be deduced from a quantity of 0·0011 g. of platinum, the results appear to have been calculated with the assumption that the formula for nicotine chloroplatinate is $(C_{10}H_{14}N_2)_2$, H_2PtCl_6. No such compound is mentioned in the literature, the most easily formed chloroplatinate being $C_{10}H_{14}N_2$, H_2PtCl_6. 0·0612 G. of this would give 0·0210 g. of platinum as compared with 0·0163 g. found by the authors.

To obtain some idea as to the nature of the substances formed in the reaction we conducted an experiment in which 2000 c.c. of 2% formaldehyde and 36 c.c. of 6·2N-ammonia mixed with 5 g. of cupric carbonate were exposed in an open glass trough to the light of a quartz mercury vapour lamp during 50 hours. The solution

was colourless after exposure but when boiled it darkened slightly. After distilling the bulk of the solution the residue was extracted with ether yielding a very small quantity of partially solid material, this was acidified, extracted with a little ether and the aqueous solution made alkaline and again extracted with ether. This ethereal solution left no visible residue on evaporation and on washing the dish with a little water and adding a drop of mercuric chloride solution, no precipitate was formed. The distillate after acidifying with hydrochloric acid and evaporating to dryness yielded a deliquescent salt in appreciable quantity. This smelt of methylamine when treated with sodium hydroxide gave the carbylamine reaction. Mercuric chloride gave no precipitate with the solution and it must be concluded that no nicotine was formed in this experiment.

A similar experiment was conducted with 500 c.c. of the solution to which 0·2 g. of nicotine was added. This was not exposed to ultraviolet light but distilled directly until the volume was reduced to 40 c.c. No nicotine could be detected in the residue. The distillate after acidifying and evaporating gave a picrate and a copious crystalline precipitate with mercuric chloride. It also contained sufficient methylamine, doubtless an impurity in the ammonia, to give the carbylamine reaction.

It is thus not possible to accept the conclusions of Bhargava and Dhar that nicotine is formed by the action of light on formaldehyde and ammonia.

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Limit of the Variation of the Relation between Intensity and Velocity of Photochemical Reactions.

By. W. V. Bhagwat.

The problem of the relation between intensity and velocity of photochemical reactions is highly controversial and attempt has been made in this paper to throw some light on the problem from theoretical considerations.

It is well known that the velocity of a reaction is determined by the number of active molecules present in the reacting system, and that the photochemical acceleration consists in increasing this number of active molecules. Amount of photochemical acceleration at any time is, therefore, a factor which is dependent on the number of inactive molecules present at any instant. Greater the number of inactive molecules, greater is the probability of activation. According to Maxwell's distribution law, always a constant fraction of the total number is in the active state, when there is no removal by chemical change. The number of active molecules is thus always a constant fraction of the total number. The simplest assumption on this basis would, therefore, be that the same fraction of the inactive molecules is activated by equal increment in intensity.

With these assumptions the author (*U. P. Akad. Sci.*, 1933, **1**, 54; *Z. anorg. Chem.*, 1931, **199**, 406) has deduced a theoretical expression for the relation between intensity and velocity of any photochemical reaction, from the view point of activation. If the intensity is varied in 'n' equal stages and A be the total number of molecules, x, the number of active molecules originally present before exposure, and y is the fraction of inactive molecules which get activated each time by exposure, then the photochemical acceleration in the first stage is proportional to $(A-x)y$, and in the nth stage is proportional to

$$(A-x)\ \{1-(1-y)^n\}.$$

It is evident from above that if the photochemical acceleration over the dark reaction is very small, y becomes very small. Moreover, y is a fraction and, therefore, less than unity. Hence the higher powers of y in the expansion of $(1-y)^n$ as squares, cubes, etc., may be neglected. The photochemical acceleration in the nth stage is, therefore, proportional to

$$(A-x)\ \{1-(1-ny)\}$$
or
$$n\ (A-x)y.$$

Hence the photochemical acceleration in the nth stage or by increasing the intensity 'n' fold is 'n' times the acceleration in the first stage. That is, when the photochemical acceleration is small, the velocity is directly proportional to the intensity. However, when y is large, higher powers of y cannot be neglected, and hence the velocity—intensity relation is less than unity or approaches square root relationship.

Thus when the absorption of the radiation is high and the reaction is not markedly photochemical in nature and the velocity of the reaction in the dark is appreciable, direct proportionality is likely to be observed. On the other hand when the reaction is highly photochemical in nature and the velocity of the dark reaction is practically negligible, square root or less than the square root relationship will be expected.

The above theoretical expression not only explains the observed results but points out one very important fact, that the relation between intensity and velocity can never exceed unity for a truly photochemical reaction, and that in practically all the photochemical reactions, there must be a tendency to show a relationship which is less than the direct. Hence all the photochemical reactions so far studied may be divided only into two classes, *viz.*,

(*i*) The reactions showing a relationship between intensity and velocity which is less than the direct, the number of such reactions being large.

(*ii*) The reactions which obey direct relationship. The author's conclusions are clearly borne out by the numerous reactions investigated by various authors mentioned in the previous paper (*U. P. Akad. Sci.*, 1933, 1, 54). As the intensity is increased, the relation between intensity and velocity falls off gradually. In short, the reactions showing direct relationship are only few. The relation

between intensity and velocity in terms of a factor greater than the direct is not to be expected from the view advanced here.

It will be observed that even the ordinary consideration of activation fails to explain the existence of a relationship greater than the direct, which means that although the number of inactive molecules available for activation is actually decreasing with the increased intensity, yet the amount of activation or the number of molecules activated for the same increase in intensity is greater in the following stage, than in the preceding one. Since that is not possible, the existence of a relationship greater than the direct seems to be improbable.

Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 493) have classified these reactions in the following three groups:

(1) Velocity tends to be directly proportional to the square of the incident radiation.

(2) Velocity tends to be proportional directly to intensity.

(3) Velocity tends to be proportional to the square root of the intensity.

The only peculiar example of the type in which more than direct relationship is observed, is found in the case of the photochemical reaction between hydrogen and chlorine, investigated by Baly and Barker (*J. Chem. Soc.*, 1921, **119**, 653). Dhar and Bhattacharya (*loc. cit.*) have obtained similar relations in case of few photochemical reactions. It is interesting to note that special attempts were made by the authors to get such relationship by decreasing the photochemical acceleration with the help of such inhibitors as potassium bromide or potassium iodide.

An alternative suggestion to explain these few exceptions which cannot be explained merely on the principle of activation of the reacting molecules has been proposed. In author's opinion the part of the absorbed energy is used up in activating the molecules and the part is lost in destroying these inhibitors and hence the whole of the absorbed energy is not responsible for the reaction, and the proportionate loss of such energy, decreases with the increase in intensity. Hence the number of molecules actually activated in the next stage is always greater than the previous stage till whole of the inhibitor is destroyed. When there is no inhibitor left, no energy will be wasted in destroying it and the number of molecules activated will be directly proportional to the amount of energy absorbed,

hence the relationship which is greater than the direct will be no more observed. This suggestion of author actually explains the observed relations in case of hydrogen and chlorine reaction and the reactions with bromine and iodine investigated by Bhattacharya and Dhar (*loc.cit.*).

The reaction between hydrogen and chlorine is highly susceptible to impurities and the photochemical combination is retarded specially by oxygen. Thus the reacting mixture of Baly and Barker contained retarding substances, which are slowly destroyed by light. That is the amount of energy required to destroy this inhibitor went on proportionately decreasing with intensity and it appears therefore, that the reacting mixture of Baly and Barker shows a photochemical acceleration, which is greater than what is expected from the intensity. In this connection it will be of interest to note the following statemant of Baly and Barker regarding the purity of their reaction mixture, "We found it very difficult to free the mixture completely from oxygen". This statement, therefore, seems to lend support to author's explanation.

Exactly similar explanation is applicable to the observations made by Bhattacharya and Dhar. Their experimental procedure shows that they have added an excess of potassium iodide or potassium bromide to suppress the photochemical acceleration. It is now an admitted fact that in bromine and iodine reactions in presence of potassium iodide or potassium bromide, KI_3 and KBr_3 molecules are formed, which act as internal filters, for the whole of the energy which is absorbed by the reactants, is not used up in activating the molecules. It is evident, therefore, that the author's explanation holds even in this case.

Thus all the photochemical reactions tend to show a relationship between intensity and velocity which is less than the direct.

Another important fact which is inherent in the expression is, that it is independent of the nature of the light source, but simply depends upon the amount of photochemical acceleration. It is usually observed that with the light of higher frequency or when the light quantum $h\nu$ is higher, the photochemical acceleration is higher, although according to Einstein's law, it should be the same. Hence, there should be greater chances of observing square root relationship in the region of higher frequency than in the region of lower frequency. The conclusion is fully supported by experiments.

Thus the present author has been able to explain the observed variation of velocity and intensity in case of photochemical reactions investigated by him and other numerous workers. The controversial problem in case of hydrogen, chlorine and other reactions has been satisfactorily explained.

SUMMARY.

1. It has been shown that the relation between intensity and velocity can show either direct relationship or a relationship which is less than the direct. From the view point of activation a relationship which is greater than the direct is improbable.

2. Only few reactions which are found to show apparently a relationship, greater than the direct, have been proved to be due to the presence of inhibitors which are destroyed by light, thereby the inhibition effect proportionately diminishing with intensity and apparently the velocity and intensity relation exceeds unity. Baly and Barker's observations regarding intensity and velocity of the photochemical reaction between hydrogen and chlorine and few of Bhattacharya and Dhar's reactions have been successfully explained.

3. It is shown that there are greater chances of observing square root relationship in a light of higher frequeney than in a light of lower frequency, a fact borne out by experiments.

My thanks are due to Prof. N. R. Dhar for his kind interest in the work.

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On Magnetic Birefringence in Mercuri-sulphosalicylic Acid Sols.

By Satya Prakash and Laxmi Narain Bhargava.

The sols and gels of mercurisulphosalicylic acid have been studied by us in previous publications (*J. Indian Chem. Soc.*, 1930, 7, 367). It was observed there that by coagulating 1% sol of mercurisulphosalicylic acid with electrolytes, transluscent or opaque jellies are obtained which undergo marked syneresis. We have now been successful in obtaining water-like transparent jellies by coagulating 2% sol. Mercurisulphosalicylic acid was prepared in the same way as described in the previous paper by dissolving well washed freshly precipitated mercuric oxide in 5-sulphosalicylic acid; the gelatinous white mass thus obtained was then dried on a water-bath. The following concentrations for the transparent jellies would be of interest.

Table I.

Mercurisulphosalicylic acid soln. (2%) = 3 c.c. Total vol. = 5 c.c.

Amount of $N/2$-KNO_3.	Observations.
0·2 c. c.	Perfectly transparent jelly in 25 hr.
0·4	Transparent jelly in 18 hr.
0·7	Transparent jelly accompained with slight opalescence in 15 hr.

By increasing the concentrations of potassium nitrate, the time of setting decreases, whilst the opalescence increases. However, it was observed by Wo. Ostwald and Mertens (*Koll. Chem Beih.*, 1926, **23**, 242) that mercurisulphosalicylic acid loses its colloidality in presence of chloride ions. The influence of chloride ions on the time of setting of this jelly are given in Table II.

TABLE II.

Amount of sol (2%) = 3 c.c. Total vol. = 5 c.c. $N/2$-KNO_3 = 1·08 c.c.

Time of setting (min.) ...	30	8	7	20	960	No jelly
Amount of $N/10$-KCl (c.c.)...	0	0·3	0·35	0·4	0·45	1·0

From these results, it would be seen that the presence of small amounts of potassium chloride sensitises the sol and the jelly is very readily obtained, while the dissolving influence begins only at a later stage. The influence of halide ions on the stability of the colloidal phase of mercurisulphosalicylic acid can be very well studied from the view point of the magnetic birefringence exhibited by the particles of this sol and hence in the present communication an attempt has been made to investigate this property of the sol under various conditions.

The phenomenon of magnetic birefringence was for the first time observed by Majorana (*R. Acad. Linci.*, 1902, *v*, **11**, 374, 463, 531) and it has been investigated by Freundlich and co-workers, Bjornstahl and others in the case of vanadium pentoxide, gold, silver, platinum and other sols. Berkman and Zocher (*Kolloid Z.*, 1927, **42**, 309, 322) observed that mercurisulphosalicylic acid exhibits the property of double refraction when in the state of flow and moreover, it is also doubly refractive when placed in an electric or magnetic field. The results of magnetic double refraction being a measure of the optical and magnetic anisotropies of the colloidal particles, are of considerable interest. Zocher and Berkman's results (*loc. cit.*) are only qualitative so far as the magnetic birefringence is concerned and as such the present study of the subject has been undertaken.

The experimental arrangement was similar to that described by by Chinchalkar (*Indian J. Phys.*, 1931, **6**, 165). A point-o-lite lamp of 1000 c. p. was used as a source, the light from which condensed and collimated before passing through the polariser of which the principal direction of vibration was inclined at 45° to the horizontal. The direction of the magnetic field as well as the neutral axis was horizontal. The sol to be investigated was placed in 33 cm. long tubes between the two poles of an electromagnet, the poles being 33 cm. wide. A long glass strip under pressure or strain was used as a compensator. The strip bent in its own plane would produce different layers above and below the neutral axis which will behave like a series of uni-axial positive and negative crystals with their axes

parallel to the neutral axis. The beam of the plane polarised light after being allowed to pass through this compensator strip is examined with a crossed nicol and a telescope attached to an Adam-Hilger micrometer eye-piece. In all the cases, a current of 8 amperes was passed through the electromagnet producing a field of 6500 gauss which was sufficient to cause marked shifts in the dark band. Nitrobenzene along with the same strained compensator was used as a standard for comparison. The readings in terms of micrometer scale are given below.

The Influence of Dilution.

The Cotton-Mouton constant for nitrobenzene has been regarded as 100 for comparison, and the values have been expressed relative to it. In the given field with the same compensator, the shift observed in the case of nitrobenzene corresponded to 108 divisions on the micrometer scale.

To some extent, the values also depend on the mode of preparing the solution of the colloid which gives particles of different dispersity, and as such in one set of experiments, one and the same sol was used. A mean of six readings was usually taken for shifts.

TABLE III.

Sol conc. (%) ...	2·0	1·0	0·5	0·4
Shift (micrometer scale) ...	100	63	28	19·5
Relative birefringence ...	92·6	58·4	25·9	18·1

These results show that in the case of this sol, the birefringence is approximately proportional to the concentration of the sol. The anomaly is more marked in the first dilutions.

TABLE IV.

Influence of Potassium Chloride.

To 10 c.c. of 2% sol varying amounts of $N/10$-KCl were added and the total volume was made up to 20 c.c. by adding water.

$N/10$-KCl ...	0	0·5	1·0	3·0
Shift ...	63	44	32	21
Relative birefringence ...	58·4	40·6	29·6	19·4

Thus as the concentration of potassium chloride is increased, the magnetic birefringence of the colloidal solution is decreased. This corresponds to the dissolving influence of chloride ions as observed by Wo. Ostwald and Martens (*loc. cit.*).

TABLE V.

Influence of Potassium Bromide.

To 10 c.c. of 2% sol varying amounts of $N/35$-KBr were added and the total volume was made up to 20 c.c.

KBr (c.c.) ...	0	0·5	1·0	2·0	3·0	5·0	10·0
Shift ...	47	41	35·	48	63	82	175
Relative birefringence ...	43·5	38·0	32·4	44 3	58·3	75·9	162·0

It will be seen from these readings, that in the presence of small quantities of potassium bromide, the anisotropy of the particles decreases, but after a concentration, the value begins to rise and goes to a considerably high length. According to the observation of Wo. Ostwald and Mertens (*loc. cit.*), the addition of bromide ions, similar to chloride ions, should bring out the dissolution of the colloidal phase. Our results on birefringence, however, show that this dissolution is only brought about at lower concentrations of bromide ions. That the sol undergoes coagulation at higher concentrations of bromide in much less time is also seen from the following results on jelly formation of the sol under the influence of bromide ions.

Amount of sol=3 c.c. Total vol.=5 c.c.

$N/2$-KBr (c.c.) ...	1·4	1·5	1·6
Time of setting ...	80′	30′	30″

TABLE VI.

Influence of Potassium Nitrate.

Amount of 2% sol=10 c.c. Total vol.=20 c.c.

$N/20$-KNO_3 (c.c.) ...	0	1·0	2·0	3·0	4 0
Shift ..	47	58	71	101	132
Relative birefringence ...	43·5	53·7	65·7	93·5	122

Influence of Barium Nitrate.

It could not be possible to study magnetic birefringence with higher concentrations of barium nitrate because the sol developed opalescence. The excessive scattering not only diminished the intensity of light but also caused the depolarisation and hence it could not be conveniently crossed by the second nicol. For this reason, the influence of very small concentrations of barium salt has been tried.

TABLE VII.

Amount of 2% sol=10 c.c. Total vol.=20 c.c.

Barium nitrate (0·05%) c.c. ...	0	1·0	2·0	3·0
Shift ...	47	47	48	50
Relative birefringence ...	43·5	43·5	44·4	46·3

The influence of small amounts of barium nitrate is very slight; however, with increased concentrations, in its presence also, as in the case of potassium nitrate, the magnetic birefringence is considerably increased.

Magnetic birefringence according to the theory of Langevin is due to the combined magnetic and optical anisotropies of the molecules. In a magnetic field, the molecules try to set themselves in places of easiest magnetisability so far as the thermal agitations allow, and on account of this tendency, if the molecules are optically anisotropic also, the medium acquires a feeble birefringence. In the case of colloidal solutions, apart from the molecular anisotropy, a sort of structural anisotropy dependent on the nature of colloidal aggregation is also exhibited.

Unless under flow, the sol of mercurisulphosalicylic acid does not show any marked optical double refraction and as such, the values obtained under the influence of magnetic field show that the particles become orientated as soon as the field is applied. Thus it is a sort of magnetic analogue of rod-like double refraction, the theory of which has been developed by Wiener (*Ber. sachs. Akad. Wiss.*, 1909, **61**, 118). The partticles of the colloids showing magnetic double refraction are non-spherical and markedly elongated, and

they are orientated in a regular manner under the influence of mechanical flow, or in magnetic or electric fields. When some salt as potassium nitrate is added to the sol, the discharged units of the colloidal particles form highly elongated chains and hence the anisotropy is very much increased in its presence.

We could not observe any birefringence in the sols of ferric phosphate or zirconium hydroxide though these are also lyophilic and capable of giving jellies. Further work is in progress of magnetic birefringence of colloidal solutions.

The authors express their indebtedness to Dr. K.S. Krishnan for providing them facilities to carry on this work in the laboratories of Indian Association for the Cultivation of Science, Calcutta.

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Studies in Tetraphenylmethane Dyes. Part II.

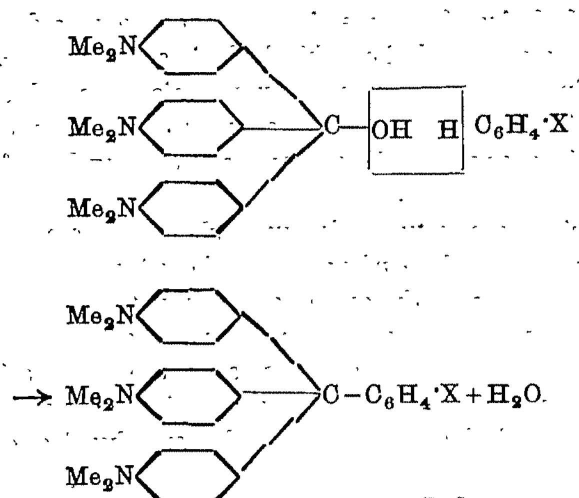
By Rajendra Nath Sen and Manas Mohan Ghosh.

Sen and Banerjee (*J. Indian Chem. Soc.*, 1931, 8, 77) prepared a few derivatives by condensing rosaniline base with aromatic amino and hydroxy compounds all of which were found to possess satisfactory dyeing properties and for which tetraphenylmethane structures were assumed.

In continuation of that work a few more compounds have now been obtained by condensing (*i*) crystal violet base and (*ii*) malachite green base with aromatic amino and hydroxy compounds. Tetraphenylmethane structure has also been ascribed to the compounds described in this paper. But this requires to be proved later on by further work.

The method adopted is the same as that of Sen and Banerjee (*loc. cit.*) *viz.*, by heating crystal violet base or malachite green base with a suitable mono or dihydroxy or aminobenzene at about 160-80° for 6-8 hours using fused anhydrous sodium acetate as the condensing agent, the yields of the products varying from 60 to 80% of theory.

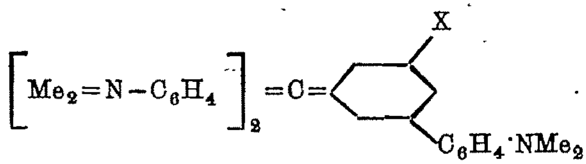
The reaction which takes place may be represented as follows:



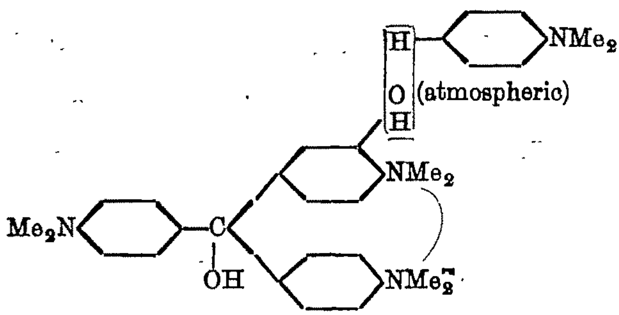
where X = OH or NH_2 or NMe_2, etc.

The hydrogen atom *para* to X reacts with the OH of the carbinol as usual.

Though these compounds cannot be represented by any quinonoid configuration in the ordinary manner, they are as good dyes as the triphenylmethane dyes; such extraordinary quinonoid structure as



is, however, conceivable. Such alternative method of condensation involving atmospheric oxidation as



does not appear very likely to take place.

The compounds derived from crystal violet may be regarded as the crystal violet base in which the carbinol 'OH' has been replaced by a phenyl residue with or without any auxochromic group and their colour is generally similar to that of crystal violet more or less modified by the additional auxochromic groups, as will be evident from the table.

In the malachite green series analogous results are obtained, the shades on silk and wool of the condensation products being influenced exactly in the same way as in the case of crystal violet.

In this connection it is interesting to note that when the condensation of crystal violet or malachite green base with salicylic acid or *o*-cresotinic acid is attempted, carbon dioxide is eliminated and the product is identical with the product obtained from phenol or *o*-cresol respectively.

As recorded by Sen and Banerjee (*loc. cit.*) it has also been found that these tetraphenylmethane derivatives undergo a marked change

of colour in acid solution in strong sulphuric acid or hydrochloric acid exhibiting from yellow to red shade which on much dilution changes from light reddish-violet to deep bluish-violet in the crystal violet series and from light greenish-blue to deep emerald green in the case of the malachite green series. No such phenomenon is, however, observed in the case of the acetic acid solution.

Experimental.

General method of preparation and purification.—1 Mol. of the base (C.V. or M. G.*) was mixed with 1½ mol. of the other component (aniline, phenol, etc.) and the mixture heated on the oil-bath till a homogeneous solution was obtained. Some fused sodium acetate was then added, the mixture well stirred, the temperature gradually raised and maintained at 160-180°. After 1 hour some more of sodium acetate was added and the heating continued for 6-8 hours with frequent stirring. When the reaction was over the excess of the second component was removed by (*i*) steam distillation (aniline, dimethylaniline, anisole, resorcin dimethylether), (*ii*) ether extraction (anisole, resorcin dimethylether) (in the C. V. series only), (*iii*) treatment with caustic soda (phenol, *o*-cresol), (*iv*) washing with water (resorcinol). Any excess of the base was removed by treating carefully with water slightly acidulated with hydrochloric acid in which the base (C. V. or M. G.) is very easily soluble while the product is not so readily soluble. The residue was then thoroughly washed, dried, and then treated with solvents.

Crystal Violet Series.

Hexamethyltetraminotetraphenylmethane, prepared from crystal violet base and aniline, separates from a mixture of alcohol and chloroform as a blue powder melting at 115-16°. It is sparingly soluble in alcohol and toluene, soluble in chloroform, acetone, benzene, carbon disulphide; insoluble in ether, petroleum ether, benzene. (Found: N, 12·32. $C_{31}H_{36}N_4$ requires N, 12·1 per cent).

The *acetyl* derivative crystallised from alcohol as a reddish violet powder, m. p. 66-68°. (Found: N, 11·3. $C_{33}H_{38}ON_4$ requires N, 11·1 per cent).

* C. V.=Crystal violet base. M. G.=Malachite green base.

p-*Hexamethyltriaminotriphenylmethylbenzene-azo-β-naphthylamine* was prepared by coupling the diazotised amine with β-naphthylamine. It separates from petroleum ether (b. p. 95°) as an orange-red powder, m. p. 116-17°. (Found: N, 13·9. $C_{41}H_{42}N_6$ requires N, 13·6 per cent).

sym-*Octamethyltetraminotetraphenylmethane*, prepared from the base and dimethylaniline, separated from alcohol and chloroform as a bluish violet powder melting at 102-4°. It is sparingly soluble in alcohol, benzene, ether, toluene; readily soluble in chloroform, acetone, carbon disulphide and insoluble in petroleum ether. (Found: N, 11·61. $C_{33}H_{40}N_4$ requires N, 11·4 per cent).

p-*Hydroxyhexamethyltriaminotetraphenylmethane*, prepared from the base and phenol, was crystallised from boiling absolute alcohol as a reddish-violet powder, m.p. 102°. It is sparingly soluble in alcohol, toluene, benzene; readily soluble in chloroform and acetone and insoluble in ether, petroleum ether and carbon disulphide. (Found: N, 9·4. $C_{31}H_{35}ON_3$ requires N, 9·03 per cent).

The *acetyl* derivative crystallised from alcohol as a light blue powder, m. p. 84-85°. (Found : N, 8·34. $C_{33}H_{37}O_2N_2$ requires N, 8·28 per cent).

2 : 4 - *Dihydroxyhexamethyltriaminotetraphenylmethene*, prepared from the base and resorcinol, crystallised from a boiling solution of alcohol and acetone as a violet powder melting above 270°. It is sparingly soluble in alcohol, chloroform, readily soluble in acetone and insoluble in benzene, ether, petroleum ether, carbon disulphide and toluene. (Found: N, 8·75. $C_{31}H_{35}O_2N_3$ requires N, 8·73 per cent).

The *benzoyl* derivative crystallised from benzene as a slate coloured powder, m.p. 117-19°. (Found: N, 6·24. $C_{45}H_{43}O_4N_3$ requires N, 6·1 per cent).

p-*Methoxyhexamethyltriaminotetraphenylmethane*, prepared from the base and anisole, crystallised from acetone as a sapphire blue powder, m.p. 140-44°. It is sparingly soluble in alcohol, acetone; moderately soluble in chloroform, benzene, toluene, carbon disulphide; insoluble in ether and petroleum ether. (Found: N, 8·98. $C_{32}H_{37}ON_3$ requires N, 8·77 per cent).

2 :4-*Dimethoxyhexamethyltriaminotetraphenylmethane*, prepared from the base and resorcin dimethylether, crystallised from alcohol as a bluish-violet powder, m.p. 122°. It is sparingly soluble in alcohol, toluene; soluble in chloroform, acetone, benzene and carbon

disulphide; insoluble in ether and petroleum ether. (Found: N, 8·4. $C_{33}H_{39}O_2N_3$ requires N, 8·25 per cent).

3-*Methyl-4-oxyhexamethyltriaminotetraphenylmethane*, prepared from the base and *o*-cresol, crystallised from boiling absolute alcohol as a bluish-violet powder, m. p. 95°. It is sparingly soluble in alcohol, benzene, toluene and carbon disulphide; readily soluble in chloroform, acetone; insoluble in ether and petroleum ether. (Found: N, 9·11. $C_{32}H_{37}ON_3$ requires N, 8·77 per cent).

The *acetyl* derivative crystallised from alcohol as a reddish-violet powder, m. p. 64-65°. (Found: N, 8·42. $C_{33}H_{39}O_2N_3$ requires N, 8·06 per cent).

Malachite Green Series.

Tetramethyltriaminotetraphenylmethane, prepared from malachite green base and aniline, crystallised from alcohol as a greenish-blue powder, m. p. 102°. It is sparingly soluble in alcohol, benzene, toluene and carbon disulphide; readily soluble in chloroform and acetone. (Found: N, 10·1. $C_{29}H_{31}N_3$ requires N, 9·98 per cent).

The *acetyl* derivative crystallised from alcohol as a buff coloured powder, m. p. 90°. (Found: N, 9·2. $C_{31}H_{33}ON_3$ requires N, 9·07 per cent).

p-*Tetramethyldiaminotriphenylmethylbenzeneazo-β-naphthylamine*, prepared by coupling the diazotised amine with β-naphthylamine, crystallised from petroleum ether (b.p. 75-95°) as a yellowish-brown powder, m. p. 160-62°. (Found: N, 12·4. $C_{39}H_{37}N_5$ requires N, 12·17 per cent).

Hexamethyltriaminotetraphenylmethane, prepared from the base and dimethylaniline, crystallised from alcohol as a bluish-green powder, m. p. 107-10°. It is sparingly soluble in alcohol, toluene and carbon disulphide; readily soluble in chloroform, acetone and benzene. (Found: N, 9·57. $C_{31}H_{35}N_3$ requires N, 9·35 per cent).

p-*Hydroxytetramethyldiaminotetraphenylmethane*, prepared from the base and phenol, crystallised from a warm mixture of alcohol and acetone as a light blue powder, m.p. 75°. It is sparingly soluble in alcohol, toluene; readily soluble in acetone, benzene, carbon disulphide and chloroform. (Found: N, 6·63. $C_{29}H_{30}ON_2$ requires N, 6·61 per cent).

The *acetyl* derivative crystallised from alcohol as a brownish-yellow powder, m. p. 93-95°. (Found: N, 6·24. $C_{31}H_{32}O_2N_2$ requires N, 6·03 per cent).

2 : 4-*Dioxytetramethyldiaminotetraphenylmethane*, prepared from the base and resorcinol, crystallised from a boiling mixture of alcohol and chloroform as a greenish ash-coloured powder, m. p. 124-26°. It is sparingly soluble in alcohol, benzene, ether and toluene and readily soluble in chloroform and acetone. (Found: N, 6·58. $C_{29}H_{30}O_2N_2$ requires N, 6·39 per cent).

The *benzoyl* derivative crystallised from benzene as a dark grey powder, m. p. 118°. (Found: N, 4·6. $C_{43}H_{38}O_4N_2$ requires N, 4·38 per cent).

p-*Methoxytetramethyldiaminotetraphenylmethane*, prepared from the base and anisole, crystallised by adding benzene to a boiling methyl alcoholic solution as a bluish-green powder, m. p. 90-95°. It is soluble on warming in benzene, carbon tetrachloride; readily soluble in alcohol, ether, ethyl acetate, acetone, chloroform and pyridine. (Found: N. 6·71. $C_{30}H_{32}ON_2$ requires N, 6·42 per cent).

2 : 4-*Dimethoxytetramethyldiaminotetraphenylmethane*, prepared from the base and resorcin dimethylether, crystallised from alcohol as a dark grey powder, m. p. 85-87°. It is sparingly soluble in alcohol and ether; readily soluble in chloroform, acetone, benzene, toluene and carbon disulphide. (Found: N, 6·27. $C_{31}H_{34}O_2N_2$ requires N, 6·01 per cent).

3-*Methyl-4-oxytetramethyldiaminotetraphenylmethane*, prepared from the base and *o*-cresol, crystallised from benzene and petroleum ether as a pea green powder melting at 113-15°. It is sparingly soluble in alcohol, acetone, benzene; readily soluble in alcohol, chloroform, toluene and carbon disulphide. (Found: N, 6·54. $C_{30}H_{32}ON^2$ requires N, 6·42 per cent).

The *acetyl* derivative crystallised from alcohol as an almond brown powder, m. p. 90-91°. (Found: N, 5·99. $C_{32}H_{34}O_2N_2$ requires N, 5·86 per cent).

TABLE.

$V=(C_6H_4 \cdot NMe_2)_3 \equiv C-$. C. V. = Crystal violet base.

Compound.	Method of preparation.	Colour and dyeing properties on silk and wool.	Remarks.
V-C_6H_4 NH_2 (I)	C. V + aniline	Bluer shade than C. V.	
V-C_6H_4·NHCOMe	Acetylation of (I)	Lighter shade than (I) (redder)	Acetylation lightens the shade.
V-C_6H_4·N = N − $C_{10}H_6NH_2$	Azo compound of (I) with β-naphthylamine	Golden yellow shade	
V-C_6H_4·NMe_2	C. V. + dimethylaniline	Blue	
V-C_6H_4·OH (II)	C.V. + phenol	Lighter shade than (I)	Methylation lightens the shade (*cf.* Sen and Banerjee. *loc. cit.*). Weaker auxochrome OH replacing the stronger auxochrome NH_2 lightens the shade.
V-C_6H_4·$OCOCH_3$	Acetylation of (II)	Blue. Much lighter than (I)	
V-C_6H_3 $(OH)_2$	C. V. + resorcin	Less bluer than (II)	
V-C_6H_4·OMe	C. V. + anisole	Redder than (II)	
V-C_6H_3·$(OMe)_2$	C. V. + resorcin dimethyl ether	Same shade as C. V.	No dyeing property as there is no auxochrome in the phenyl residue, no effect of Me group.
V-C_6H_3(OH) (Me) (III)	C. V. + *o*-cresol	Same shade as (II)	
V-C_6H_3(OCOMe) (Me)	Acetylation of (III)	Less blue than (III)	

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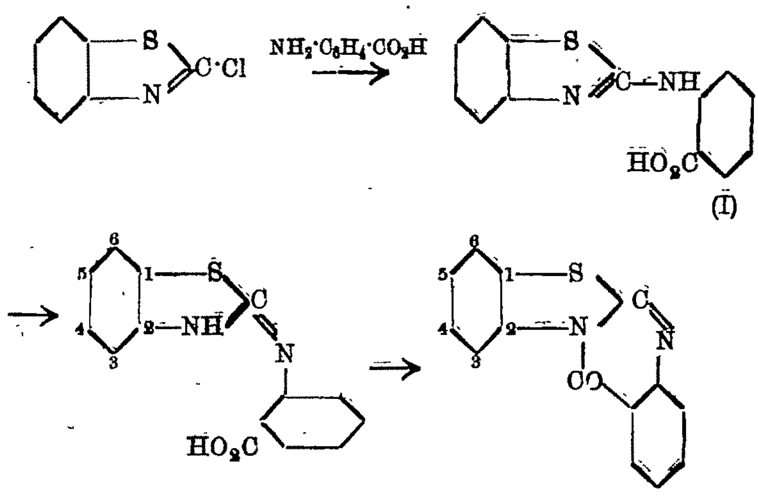
Benzthiazoloneyl Quinazolines.

By Prafulla Kumar Bose and Kumud Behari Pathak.

Complex heterocyclic systems containing the quinazoline ring have been synthesised by Asahina, Manske and Robinson (*J. Chem. Soc.*, 1927, 1708) and by Aggarwal and Rây (*J. Indian Chem. Soc.*, 1929, **6**, 723) by the method of Sen and Rây (*J. Chem. Soc.*, 1926, 646), which consisted in condensing suitable cyclic amides with anthranilic acid in presence of phosphorus trichloride. This method, however, failed in the case of α-hydroxyquinolines, but by replacing the hydroxyl group by of chlorine, the desired results were obtained (Bose and Sen, *J. Chem. Soc.*, 1931, 2840). This modified method has now been applied to fuse a quinazoline ring to benzthiazoles, thus:



(I)

(II) (III)

The benzthiazoloneyl quinazolines (III), thus obtained, are stable compounds and can be easily nitrated. The intermediate acids could not be isolated from the reaction products, but they are indirectly obtained by hydrolysis of (III). The substances are expected to be physiologically active.

EXPERIMENTAL.

The chlorobenzthiazoles used in this investigation were prepared by the method of Hofmann, the yields being generally poor (*Ber.*, 1879, **12**, 1126).

1-*Chlorobenzthiazole and anthranilic acid*: *Formation of* (III).—Molecular quantities of the components were carefully heated over a small flame, which was withdrawn as soon as the reaction became vigorous. The horny mass obtained on cooling was extracted with ammonia to remove any unchanged anthranilic acid. The insoluble residue was crystallised from a mixture of pyridine and alcohol. It formed slender needles, m.p. 189°. (Found: C, 66·48; H, 3·12; N, 10·9; S, 12·5. $C_{14}H_8ON_2S$ requires C, 66·6; H, 3·17; N. 14·1; S, 12·7 per cent).

Hydrolysis of above: *Formation of* (I) *or* (II).—The substance (0·4 g.) was refluxed with 25 c.c. of 5% alcoholic potassium hydroxide for 3 hours. The solution was acidified with acetic acid and the precipitate crystallised from acetone as colourless needles, m.p. 187°. The substance is acidic to litmus and decomposed sodium bicarbonate in the cold. (Found: N, 10·39. $C_{14}H_{10}O_2N_2S$ requires N, 10·37 per cent). Acetic anhydride converted it into the parent substance (III) by extracting a molecule of water. The *sodium salt* was prepared by treating an alcoholic solution of the acid with alcoholic sodium hydroxide. On recrystallisation from alcohol it melted at 273°. (Found: Na, 7·8. $C_{14}H_9O_2N_2SNa$ requires Na, 7·9 per cent).

Nitration of (III).—To a cooled mixture of 1 c.c. fuming nitric acid and 1 c.c. concentrated sulphuric acid was gradually added 0·5 g. of the substance. After a few minutes the yellow solution was poured into crushed ice and the precipitate collected. It formed yellow needles from hot acetic acid, m.p. 279-80°. (Found: N, 16·65. $C_{14}H_6ON_2S(NO_2)_2$ requires N, 16·4 per cent).

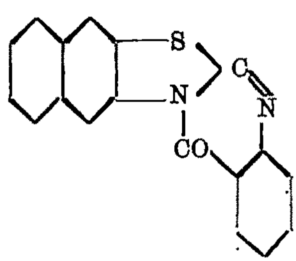
1-Chloro-5-methylbenzthiazole was prepared by Hofmann's method and was obtained as colourless needles from cold methyl alcohol, m.p. 42°. Hunter (*J. Chem. Soc.*, 1930, 2206) described this substance as an oil, b.p. 148-52°/15 mm. On condensation with anthranilic acid, the corresponding benzthiazoloneyl quinazoline was obtained as colourless needles, m.p. 226°. (Found: C, 67·63; H, 3·77; N, 10·43. $C_{15}H_{10}ON_2S$ requires C, 67·66; H, 3·75; N, 10·5 per cent). Hydrolysis with alcoholic alkali led to the formation of a crystalline

acid, m.p. 188-89°. (Found: N, 9·56. $C_{15}H_{12}O_2N_2S$ requires N, 9·8 per cent). It could be converted into the original compound by the action of hot acetic anhydride. The *sodium salt* melted at 280°. (Found: Na, 7·71. $C_{15}H_{11}O_2N_2SNa$ requires Na, 7·51 per cent). *Nitration* with a mixture of fuming nitric acid and sulphuric acid in the cold gave rise to two compounds: (*i*) A *dinitro*-compound, m.p. 280°, which separated from acetic acid as yellow star-like crystals, and (*ii*) a *mononitro*- compound which was less soluble in acetic acid and formed yellow needles from acetone, m.p. 304°. [Found: (*i*) N, 15·9. (*ii*) N, 13·7. $C_{15}H_8ON_2S(NO_2)_2$ requires N, 15·7 per cent. $C_{15}H_9ON_2S(NO_2)$ requires N, 13·5 per cent].

1-*Chloro-3-methylbenzthiazole.*—Attempts to prepare this by Hofmann's method (temperature range 130°-170°) or by Hunter's modification of the same method (*J. Chem. Soc.*, 1925, 1488) were not successful. By Sandmeyer's reaction the chlorobenzthiazole was obtained from the corresponding aminothiazole, but the yield was too poor to enable us to study its condensation with anthranilic acid.

1-Chloro-4-methylbenzthiazole and anthranilic acid gave the usual product crystallising as colourless needles from a mixture of pyridine and alcohol, m.p. 180°. (Found: N, 10·53. $C_{15}H_{10}ON_2S$ requires N, 10·52 per cent). The corresponding *acid* melted at 189°. (Found: N, 9·5. $C_{15}H_{12}O_2N_2S$ requires N, 9·8 per cent).

α-*Naphthothiazoloneyl Quinazoline.*



It was obtained in the form of colourless prisms (m.p. 261°) by condensing 1-chloro-α-naphthothiazole (m.p. 75°) with anthranilic acid in the usual way. (Found: N, 9·25. $C_{18}H_{10}ON_2S$ requires N, 9·27 per cent).

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Derivatives of *m*-Cresotic Acid.

By Narshing Muljibhai Shah and Rupchand Lilaram Alimchandani.

Schleussner and Voswinckel (*Annalen*, 1921, **422**, 111) reported that chloral condensed with *m*-cresotic acid in the *meta* position to the hydroxyl group. Although in their products the *para* position, which is surely not unfavourable to condensation, is supposed to be vacant, they were unable to carry the condensation beyond the first stage.

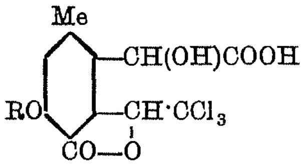
It is now found by the present authors that chloral condenses with 4-hydroxy-5-carboxy-2-methylmandelic acid (I, R=H) (*J. Indian Chem. Soc.*, 1931, **8**, 266) and with its methyl ether (I, R=Me) (Meldrum and Alimchandani, *ibid.*, 1929, **6**, 256).

The hydroxy condensation product could not be purified ; the methyl ether product has been purified, analysed and further examined. It might have the constitution (V) or (VII) if *m*-cresotic acid and its derivatives have any tendency to condense with chloral in the *meta* position to the hydroxyl or methoxyl group. The constitution (V) is out of consideration because the substance, when heated with sulphuric acid, does not give the aldehyde (VI). The constitution (VII) is wrong because the substance (*a*) on hydrolysis, gives the original mandelic acid (I, R=Me), (*b*) on reduction, gives the substance (III, R=Me) which on treatment with sulphuric acid gives 2-methyl-4-methoxy-5-carboxybenzaldehyde (IV, R=Me) (Meldrum and Alimchandani, *loc. cit.*), (*c*) on oxidation, gives *a*-coccinic acid and not cochinillic acid. Thus the evidence is that chloral does not condense with *m*-cresotic acid or its derivatives in the *meta* position to the hydroxyl group.

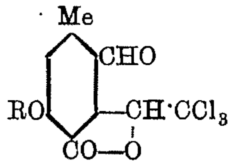
All the reactions indicate that the condensation product is the chloralide (II, R=Me). The reduction product (III) is a mixed ether in which one of the radicals is derived from the alcohol $HO{\cdot}CH_2{\cdot}CHCl_2$. There is a possibility of a double bond in the side-chain of (III) of the type $-CH:CCl_2$. But this has been excluded on the grounds (*i*) of the results of analysis and (*ii*) that it does not

absorb bromine. Meldrum and Kapadia (*J. Indian Chem. Soc.*, 1932, **9**, 483) have also described similar reduction products containing the group $-CH_2 \cdot CHCl_2$.

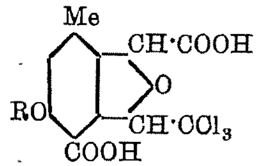
Other ethers obtained similarly from various chloralides and derived from the alcohol $-HO \cdot CH_2 \cdot CHCl_2$ will be described in a subsequent paper.



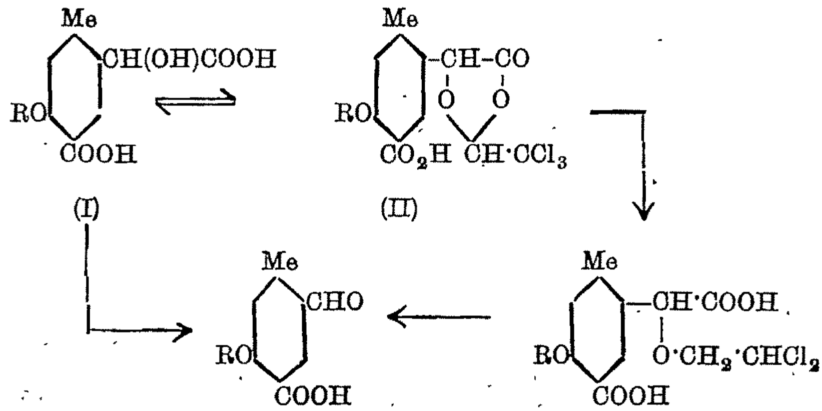
(V)



(VI)



(VII)



(IV) (III)

Experimental.

4-Methoxy-5-carboxy-2-methylmandelic acid chloralide (II, R=Me).—4-Methoxy-5-carboxy-2-methylmandelic acid (I, R=Me) (10 g.), chloral hydrate (14 g.) and sulphuric acid (30 c.c.) were mixed and the clear solution, obtained on shaking, was kept for 5-6 days. The reaction mixture was then poured into ice when a white solid separated, which was collected, washed and dried on a porous plate. It was crystallised from ethyl acetate as rhombic crystals, m.p. 178-79°. (Found: Cl, 28·91. $C_{13}H_{11}O_6Cl_3$ requires Cl, 28·81 per cent). It is very soluble in acetic acid, acetone, ether; soluble in ethyl acetate, chloroform and petrol.

Hydrolysis of the chloralide.—The chloralide (8 g.) was boiled with a solution of barium hydroxide (10 g. in 150 c.c. of water) for about an hour. The solution, when evaporated to a small bulk, deposited silky clusters of needles which were found to be the barium salt of the original mandelic acid (I).

Reduction of the chloralide.—To the hot solution of the chloralide (5 g.) in glacial acetic acid (50 c.c.), zinc dust was added slowly. After the reduction was over, the solution was filtered to remove unchanged zinc and the filtrate was diluted with water. On rubbing with a glass rod, a white substance was obtained which was found to be a zinc salt. On treating with hydrochloric acid, the reduction product was obtained. It crystallised from dilute methyl alcohol as needles, m.p. 195-96°. (Found: C, 45·94; H, 4·00; Cl, 21·27. $C_{13}H_{14}O_6Cl_2$ requires C, 46·30; H, 4·16; Cl, 21·04 per cent. Unsaturated formula $C_{13}H_{12}O_6Cl_2$ requires C, 46·58; H, 3·58; Cl, 21·17 per cent).

The reduction product (III, 1 g.) was dissolved in chloroform and bromine (0·5 g.) dissolved in the same solvent, was added. The colour of the bromine was not discharged even on keeping for 24 hours, indicating that the reduction product was a saturated substance. On evaporating the solvent, the original product was obtained. Dry ether was anbstituted as a solvent with the same result.

Action of sulphuric acid on the reduction product.—The reduction product (1 g.) was heated with 20 c.c. of sulphuric acid on the water-bath; hydrochloric acid gas was evolved. On adding the cold reaction mixture to water, a white substance separated, which after crystallising from water was found to be identical with 4-methoxy-5-carboxy-2-methylbenzaldehyde (IV, R=Me) (Meldrum and Alimchandani, *loc. cit.*).

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Induced and Photochemical Oxidation of Sodium Tartrate by Air and its Use in Diabetes and Prolonged Fasting.

By C. C. Palit and N. R. Dhar.

In several publications (*J. Phys. Chem.*, 1925, **29**, 926; 1928, **32**, 1263; 1930, **34**, 711, 993; 1932, **36**, 2504; *Z. anorg. Chem.*, 1930, **191**, 150) we have shown that in presence of inductors like ferrous hydroxide, cerous hydroxide, manganous hydroxide, glutathione, insulin, etc., which can take up oxygen directly from air under ordinary condition, solutions or suspensions of food materials like starch, sugars, proteins (egg-yellow, egg-white, milk, amino acids etc.), fats (butter, lecithin, etc.), glycogen and glycerol can be readily oxidised by passing air at the ordinary temperature. Moreover, it has been shown that solutions or suspensions of these food materials can be oxidised to carbon dioxide and water by simply passing air in presence of sunlight. In presence of sunlight, the induced oxidation of food materials is greatly increased.

In this paper, we are recording the experimental results obtained in the oxidation of sodium tartrate in presence of inductors like ferrous hydroxide or cerous hydroxide by passing air through its solutions and also the results obtained in presence of alkali, alkali carbonate, alkali bicarbonate and alkali sulphite respectively in (*i*) diffused light and (*ii*) sunlight.

In these experiments, a slow current of air, free from carbon dioxide, is passed through a bottle containing the solution of sodium tartrate. Each of these bottles contained freshly prepared 0·1069 g. of cerous hydroxide or 0·06476 g. of ferrous hydroxide. In each case 10 c.c. of the tartrate solution are added to the inductor and the total volume is then made up to 100 c.c. and a known volume of air was allowed to bubble slowly through the mixture. After passing the requisite amount of air the mixture is treated with a saturated solution of potassium sulphate to coagulate the hydroxide, filtered and washed with water containing potassium sulphate till free from tartrate. The filtrate containing the unoxidised tartrate is concentrated to a small volume (10 c.c.) and heated with 5 g. of potassium

chloride and 5 c.c. of glacial acetic acid (99—100%). The tartrate is then precipitated as bitartrate by the addition of 50-60 c.c. of absolute alcohol. The precipitate of potassium bitartrate is allowed to settle for 2 hours and filtered and washed well with absolute alcohol free from acid. The precipitate is dissolved in hot water and the solution is titrated with a standard solution of caustic soda, using phenolphthalein as indicator. From the amount of alkali required, the quantity of tartrate remaining unoxidised is estimated. The following are the experimental results.

TABLE I.

In each of these experiments, 0·06476 g. ferrous hydroxide or 0·1069 g. cerous hydroxide was taken. 1 C.c. of $N/10$-NaOH=0·0194 g. of Na-tartrate. 10 c.c. of solution of Na-tartrate =5·1 c. c. of $N/10$-NaOH=5·1 × 0·0194=0·0989 g. of Na-tartrate.

Inductor.	Vol. of air passed.	Duration of air passed.	Amt. of Na-tart. left after the expt. in terms of $N/10$-NaOH.	Amt. of Na-tart. oxidised in terms of $N/10$-NaOH.	Na-tart. oxidised.
Cerous hydroxide	36·5 litre	18 hr.	2·95 c.c.	2·15 c.c.	42·15%
"	73·0	30	2·10	3·00	58·8
Ferrous hydroxide	36·5	18	3·95	1·15	22·03
"	73·0	30	3·20	1·90	37·3

From the results in Table I, it is seen that the amount of sodium tartrate oxidised is greater with cerous hydroxide than with ferrous hydroxide used as inductor and that the amount of oxidation increases with the increase of volume of air which is passed through the mixture.

In order to find out whether cupric hydroxide when added in varying amounts to the inductors, would accelerate or retard the oxidation of sodium tartrate, we have carried on some experiments by adding 5 c.c. of copper sulphate solution of varying concentrations to solutions of ferrous sulphate or cerous chloride and the mixture precipitated as hydroxides by the addition of an equivalent amouut of caustic soda. These mixed hydroxides are then used as

inductors in the oxidation of sodium tartrate. The following are the experimental results.

TABLE II.

In each of these experiments, 20 c.c. of $FeSO_4 \equiv 0.06476$ g. $Fe(OH)_2$ or $CeCl_2 \equiv 0.1069$ g. $Ce(OH)_3$ were taken to which 5 c.c. of $CuSO_4$ were added and then precipitated as hydroxides by the addition of equivalent amount of alkali. 10 C.c. of Na-tartrate soln. $= 5.1$ c.c. of $N/10$-NaOH.

Inductor.	Vol. of air passed.	Duration of air passed.	Amt. of $CuSO_4$ added in 5 c.c. of the soln. added.	Amt. of Na-tart. left after the expt. in terms of $N/10$ NaOH.	Amt. of Na-tart. oxidised in terms of $N/10$ NaOH.	Na-tartrate oxidised.
$Ce(OH)_3$ and $Cu(OH)_2$	36·5 litre	13 hr.	0·05 g.	3·5 c.c.	1·6 c.c.	31·37%
	,,	,,	0·025	2·7	2·4	47·06
	73·0	30	0·0025	1·7	3·4	66·7
$Fe(OH)_2$ and $Cu(OH)_2$	36·5	13	0·05	4·2	0·9	17·6
	,,	,,	0·025	3·5	1·6	31·4
	73·0	30	0·0025	2·6	2·5	49·02

From Table II, we find that the amount of oxidation of sodium tartrate is greatly accelerated by the addition of very small quantity of copper. On comparing the results given in Tables I and II it is seen that copper, when present in greater quantity acts as a marked retarder, whilst it acts as an accelerator when present in minute quantity. We have also investigated the influence of mild and strong alkali on the oxidation of sodium tartrate without any inductor in presence or absence of sunlight. The following results are obtained.

TABLE III.

Experiments in diffused light.

In each of these experiments, 10 c.c. of sodium tartrate solution were taken to which a definite weight of strong or mild alkali was added and air was passed into the solution. The volume of air passed=20 litres in 7 hours. 10 C.c. of sodium tartrate solution=

5·1 c.c. of $N/10$-NaOH.

Substance used.	Amt. of substance added in 10 c.c. of the soln.	Amt. of Na-tart. left after the expt. in terms of $N/10$-NaOH.	Amt. of Na tart. oxidised in terms of $N/10$-NaOH.	Na-tart. oxidised.
1. Caustic soda	0·04 g.	4·85 c.c.	0·25 c.c.	4·9%
2. Sodium carbonate	0·10	4·90	0·20	3·92
3. Sodium bicarbonate	0·10	4·95	0·15	2·94
4. Sodium sulphite	0·10	4·80	0·30	5·9

TABLE IV.

Experiments in presence of sunlight.

10 C.c. of solution of sodium tartrate=5·1 c.c. of $N/10$-NaOH.
Volume of air passed=20 litres in 7 hours.

Substance used.	Amt. of substance added in 10 c.c. of the soln.	Amt. of Na-tart. left after the expt. in terms of $N/10$-NaOH.	Amt. of Na tart. oxidised in terms of $N/10$-NaOH.	Na-tart. oxidised.
1. Caustic soda	0·04 g.	4·1 c.c.	1·0 c.c.	19·6%
2. Sodium carbonate	0·10	4·2	0·9	17·6
3. Sodium bicarbonate	0·10	4·3	0·8	15·6
4. Sodium sulphite	0·10	3·8	1·3	25·5

The above results (Tables III and IV) show that the amount of oxidation of sodium tartrate is greater in presence of sunlight than that in its absence under the same conditions. The order of oxidation of sodium tartrate in presence of alkali or alkali salts in both the cases is the following:—sodium sulphite>sodium hydroxide> sodium carbonate>sodium bicarbonate

Sodium sulphite acts also as an inductor and that is why the amount of oxidation is greatest in its presence. The foregoing results obtained in light show that in presence of sunlight the amount of tartrate oxidised is greater than in the diffused light of the laboratory. It is known that visible light, specially rays of longer wave-lengths, can penetrate the epidermis to appreciable depths and

hence it has been suggested that light acts as a preventive and curative agent in diseases by acting not only as a stimulant of the body cells but also as an accelerator in the metabolism of food materials (compare Dhar, "New Conceptions in Biochemistry," 1932).

From these results, it appears that tartrates are oxidised both in presence of light or inductors. Hence it seems that in the animal body tartrates may act not only as buffers in maintaining the alkalinity of the system but they can also supply energy acting as food material.

TABLE V*a*.

Estimation of potassium oleate oxidised by the addition of small quantity of inductors—ferrous (≡0·00648 g.) or cerous hydroxide (≡0·01069 g.)—in presence or absence of sodium tartrate.

To each of these hydroxides 20 c.c. of 1% solution of potassium oleate added. The volume of air passed = 78 litres in 30 hrs. 20 C.c. of sodium tartrate solution = 10·3 c.c. of *N*/10-caustic soda = 0·1998 g. of sodium tartrate.

Amount of absorption of ICl_3 by fat in terms of *N*/10-sodium thiosulphate before the experiments (blank) = 11·3 c.c.

Inductor.	Amt. of Na-tartrate added.	Amt. of absorption of ICl_3 by fat left after the expt. terms in of *N*/10-thio.	Amt. of fat oxidised in terms of *N*/10-thio.	Amount of fat oxidised.
Cerrous hydroxide	0·0000 g.	6·2 c.c.	5·1 c.c.	45·1%
	0·1998	9·4	1·9	16·8
Ferrous hydroxide	0·0000	6·7	4·6	40·7
	0·1998	10·4	0·9	7·9

TABLE V*b*.

Estimation of sodium tartrate oxidised by the addition of small quantity of inductors under identical conditions as in Table V*a* in presence or absence of potassium oleate.

Amount of sodium tartrate taken in 20 c.c. of the solution before experiment in terms of-*N*/10 caustic soda (blank) = 10·3 c.c.

Inductor.	Amt. of K-oleate added.	Amt. of Na-tart. left after the expt. in terms of $N/10$-NaOH.	Amt. of Na tart oxidised in terms of $N/10$-NaOH.	Na-tart. oxidised.
Cerous hydroxide	Nil	6·7 c.c.	3·6 c.c.	34·95%
	20 c.c.	8·6	1·7	16·5
Ferrous hydroxide	Nil	8·2	2·1	20·3
	20	8·8	1·5	14·6

The experimental results show that by the addition of sodium tartrate, the amount of potassium oleate oxidised in 30 hours by 73 litres of air is considerably decreased. In the case of ferrous hydroxide as inductor, in presence of sodium tartrate the percentage of potassium oleate oxidised is 7·9, whilst under identical conditions and in absence of sodium tartrate, the percentage is 40·7. The corresponding results with cerous hydroxide as inductor are 16·8% and 45·1% respectively. Hence it is clear that the addition of a tartrate markedly decreases the velocity of the oxidation of potassium oleate. Moreover, the presence of oleate retards the velocity of the oxidation of sodium tartrate.

These results seem important from the point of view of treatment of diabetes and prolonged fasting. Under normal conditions, the heat and energy of the body are derived from the simultaneous combustion of carbohydrates, fats and possibly of proteins. When, as a result of special conditions, such as diabetes, carbohydrate is not burning, more fat and possibly protein must be burnt in order to maintain the body temperature and activity at its normal level. Hence in unit time, more fat would be burning than under normal conditions, and the combustion of fat would be incomplete, so that acetone bodies would be formed. Chakravarti and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 617) have observed that in the rapid oxidation of fatty acids by hydrogen peroxide and ferric salts, there is a formation of acetone bodies. They have also observed that if the rate of oxidation of fats be slowed down, as the case when carbohydrates (*e.g.*, glucose) are present, the amount of acetone bodies formed diminishes. Palit and Dhar (*J. Phys. Chem.*, 1930, **34**, 710) further find that, in the slow and induced oxidation of fats, acetone bodies are not formed at all, but only carbon dioxide and water, the products of normal metabolism.

The experimental results recorded here and in previous publications show that just as carbohydrates decrease the velocity of oxidation of the fats, similarly tartrates can also decrease the velocity of the oxidation of fat. Hence a tartrate or a citrate, apart from its power of acting as a buffer in removing the excessive hydrogen ion (H°) generated in the body, may serve as an anti-ketogenic substance like a carbohydrate.

The authors are of opinion that the tartrates or citrates in the drinks will prove beneficial in the treatment of long continued fasts, because in such cases the body has not lost the power of oxidation and will utilise the tartrates and citrates as food along with the fats of the body.

Our experimental results show that in presence of traces of copper, the induced oxidation of tartrate is markedly facilitated, whilst in larger concentrations, it retards the same process. Hence it appears that in the treatment of metabolism diseases or anaemia, the addition of traces of copper salts to iron or manganese may be useful.

SUMMARY.

1. Sodium tartrate is oxidised by air in presence of inductors like ferrous hydroxide or cerous hydroxide and the amount of oxidation is greater with cerous hydroxide than with ferrous hydroxide. The amount of oxidation increases with the amount of air passed.

2. It has been found that copper salts when present in minute quantity accelerate the induced oxidation of sodium tartrate but when present in larger quantity they act as retarders.

3. Sodium tartrate can be oxidised both in presence or absence of sunlight by passing air through its solution when mixed with strong or mild alkali. The amount of oxidation is greater in light than in its absence.

4. Light in the treatment of disease, is likely to act as a stimulant of body cells and accelerator of metabolism.

5. The experimental results show that tartrates may act not only as buffers in maintaining the alkalinity of the system but can also supply energy serving as food material.

6. It is suggested that a mixture of sodium tartarte or citrate and sodium bicarbonate is likely to be more efficacious in the treatment of diabetes and long continued fasting than sodium bicarbonate alone.

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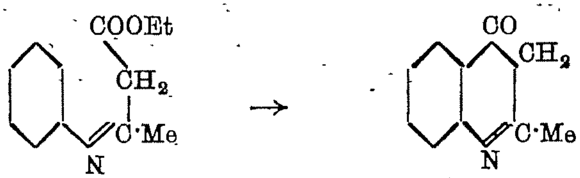
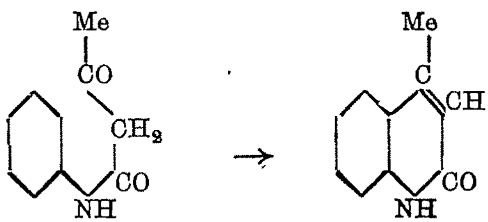
Preparation of *sym*-Acylarylureas.

By Nirmalananda Palit.

The present work arose from an attempt to study the parallelism in reactions between acetoacetic ester and acetylurethane. The former with aniline gives two classes of products according to the temperature of reaction, an anil (I) and an anilide (II), both of which easily undergo ring-closure with sulphuric acid thus:



(I)



(II)

Acetylurethane has a similar constitution to β-ketonic ester and behaves analogously with phenylhydrazine as observed by Andreocci (*Gazzetta*, 1889, **19**, 448). This led Clark (*J. Chem. Soc.*, 1898, **73**, 865) to investigate if it also behaves similarly with aniline to form anils and anilides as above, and he found that in all his experiments, although no anil formation could be detected, the anilide was formed. The present work aimed to stretch the analogy a little further by trying to effect a ring-closure in the anilide and thereby synthesise the hitherto unknown methyl-α-quinazolone

$$Me\cdot CO\cdot NH\cdot CO\cdot NH\cdot Ph \longrightarrow C_6H_4\begin{cases} C(Me) = N \\ NH \;\; - \;\; CO \end{cases}$$

The task proved to be very difficult and large quantities of (III) were needed to make an exhaustive attempt, the results of which will be communicated later. Clark's tediously slow process of heating acetylurethane with alcoholic aniline in sealed tubes gave only 60% yield. The yield of acetylurethane by Moreath's process (*Ber.*, 1875, **8**, 1182) is also not good. It has been found, however, that acetylurea which can be obtained in a quantitative yield from urea (Werner, *J. Chem. Soc.*, 1916, **109**, 1127) on heating with aniline at 170° gave acetylphenylurea in good yield. Walther and Wlodkowski prepared this as well as acetyl-*p*-tolylurea and benzoylphenylurea by the action of the acyl chlorides on the arylureas in hot pyridine, but they represented each of them to be unsymmetrical (*aa*-substituted) ureas, $NH_2 \cdot CO \cdot N(R)COR'$. The compounds, prepared in the present investigation, have been found to be identical with Walther and Wlodkowski's compounds and hence their compounds were in fact symmetrical.

After the extraction of acetylphenylurea with hot water a residue was obtaind (m. p. 235-36°) which was stable towards boiling acid and alkali and which gave with hot hydrochloric acid traces of aniline. This was identified to be diphenylurea and its production simultaneously with acetylphenylurea suggests that the latter breaks up on prolonged heating into phenyl carbimide which unites with a further molecule of aniline thus:

$$Me \cdot CO \cdot NH \cdot CO \cdot NH \cdot Ph \longrightarrow Me \cdot CO \cdot NH_2 + O:C:NPh$$

$$Ph \cdot NC:C:O + NH_2 \cdot Ph \longrightarrow Ph \cdot NH \cdot CO \cdot NH \cdot Ph.$$

Acetamide has been isolated in the products of the reaction. The proportion of acetylphenylurea, diphenylurea, acetamide and unchanged acetylurea in the melt was approximately 68·5, 11·4, 14·2 and 5·5% respectively. It may be mentioned here that acetylurea itself is known to decompose on heating to give cyanuric acid. Presumably then, it first decomposes into acetamide and *iso*cyanic acid, the latter polymerising into cyanuric acid.

$$Me \cdot CO \cdot NH \cdot CO \cdot NH_2 \longrightarrow Me \cdot CO \cdot NH_2 + NH:C:O$$

$$3\,NH:C:O \longrightarrow C_3N_3(OH)_3$$

If the acetamide in the present investigation arose from a primary decomposition of the starting material, a simultaneous formation of monophenylurea ought to result from a condensation of

*iso*cyanic acid with the aniline present. The absence of this and the formation of diphenylurea instead, substantially corroborates the view of the mechanism of reaction previously mentioned.

In the above experiment, aniline was successfully replaced by *p*-toluidine and *p*-anisidine to give yet better yields of *sym*-acetyl-*p*-tolyl and acetyl-*p*-anisylurea. In these cases, the evolution of ammonia was very energetic and the reaction was complete within a much shorter period and if the heating was continued further the yield of acylarylurea was diminished and complex by-produts began to appear. Thus acetylurea and *p*-toluidine when heated at 170-75° for 3 hours gave a melt which was practically acetyl-*p*-tolylurea alone but if the heating was continued for 2 hours more, its propor tion fell down to 30% with a simultaneous appearance of *p*-ditolyl-urea.

With *p*-anisidine the effect of heat was still more interesting. Thus at 175-80° for 2 hours, acetylurea and *p*-anisidine gave a melt comprising of 69% of acetyl-*p*-anisylurea, 10 % of *p*-dianisyl-urea and 20 % of unchanged acetylurea. If the heating was prolonged for 2 hours more, no unchanged acetylurea could be observed in the melt while the proportion of dianisylurea considerably increased. Curiously further, acetylanisylurea was totally absent and was replaced by two more compounds, one of which was identified to be monoanisylurea and the other had an empirical formula $C_{13}H_{13}O_3N_2$.

In extending the reaction to the case of benzoylurea, all the three amines reacted vigorously to give excellent yields of benzoyl-arylureas practically without the formation of any by-product. The above method thus proved to be a very easy and quick method for the preparation of symmetrically substituted acylarylureas from cheap starting materials.

Experimental.

Reactions of Acetylurea.

(*a*) *With aniline.*—Finely powdered acetylurea (5 g.) soaked with aniline (4·5 g.), was heated in an oil-bath at 170-75° for 5 hours, when ammonia was evolved. The melt was poured in a porcelain basin and the solid (9 g.) thoroughly powdered and digested with warm water for a few minutes. The water extract gave on eva-

poration needles of unchanged acetylurea (0·4 g.), which crystallised from alcohol and melted at 217-18°. The alcoholic mother liquor on evaporation gave a viscous oil rapidly solidifying to acetamide (1 g.).

The residue (7·2 g.) was repeatedly extracted with large volumes of boiling water. The acetylphenylurea crystallised in light fern-like mass, m. p. 183°, yield 4·8 g. (Found: N, 15·91. $C_9H_{10}O_2N_2$ requires N, 15·73 per cent). The portion which did not dissolve in hot water was nearly pure diphenylurea. It was obtained from alcohol in small slender needles (0·8 g.), m. p. 235-36°. (Found: C, 73·43; H, 5·66; N, 8·64. $C_{13}H_{12}ON_2$ requires C, 73·58; H, 5·66; N, 8·49 per cent).

(*b*) *With* p-*toluidine*.—Equal quantities (3 g.) of both were heated to 215-20° till acetylurea melted and formed a homogeneous mixture. The temperature was then lowered down and maintained at 170° for 5 hours. Finally the temperature was raised to 210° to melt it once more. The acetyl-*p*-tolylurea was extracted with hot water and crystallised from alcohol in needles, m. p. 199-200°, yield 1g. (Found: N, 14·62. $C_{10}O_{12}O_2N_2$ requires N, 14·58 per cent). The residue was ditolylurea (2 g.). It was crystallised from excess of acetone and alcohol, m. p. 260°. (Found: N, 11·92. $C_{15}H_{16}ON_2$ requires N, 11·66 per cent).

In repeating the experiment, the mixture was heated at 170° for 3 hours only. The acetylurea gradually dissolved in the melt and needles separated on the cooler parts. The crude mass on two crystallisations from alcohol gave acetyl-*p*-tolylurea in clusters of needles.

(*c*) *With* p-*anisidine*.—The mixture of acetylurea (3 g.) and *p*-anisidine (3 g.) was maintained at 185-90° for 4 hours. The cooled melt was soft and sticky and was digested with hot dilute hydrochloric acid. The extract on adding alkali gave a precipitate which crystallised in plates from water. This was anisidineurea (0·8 g.), m. p. 168°. (Found: N,16·76. $C_8H_{10}O_2N_2$ requires N, 16·87 per cent). The residue from the dilute acid was crystallised from an excess of alcohol in purple needles, m. p. 220-21°. (Found: C, 64·02; H, 5·62; N, 11·48. $C_{13}H_{13}O_3N_2$ requires C, 63·67; H, 5·30; N, 11·16 per cent). The portion which did not dissolve in alcohol was crystallised from a large excess of amyl alcohol in long flat white needles of dianisylurea, m. p. 235-37°. (Found: N, 10·46. $C_{15}H_{16}O_3N_2$ requires N, 10·29 per cent).

In repeating the experiment the first evolution of ammonia was noticed at 180° and the mixture was maintained at this temperature for 2 hours only. The cooled melt was not sticky and on digestion with warm water for a couple of minutes gave the unchanged acetylurea (1·2 g.). The residue on repeated extraction with boiling water gave a wooly mesh of light needles of acetylanisylurea (4 g), m. p. 172°. (Found: N, 13·58. $C_{10}H_{12}O_3N_2$ requires N, 13·45 per cent). The undissolved portion was dianisidylurea.

Reactions of Benzoylurea.

Benzoylurea (3·2 g., prepared in a quantitative yield according to the latest improved method of Ostrogovich, *Chem. Zentr.*, 1930, I, 889 and better crystallised from pyridine instead of alcohol in light shining flakes) and aniline (1·8 g.) began to evolve ammonia at 170°. The evolution ceased after 1½ hours and although the mixture was never a complete melt, the flakes of benzoylurea were replaced by minute needles which crystallised beautifully from amyl alcohol in a white mesh but was not pure (3 g.). Glacial acetic acid was a better solvent for purification, m. p. 204-5°. (Found: N, 11·82. $C_{14}H_{12}O_2N_2$ requires N, 11·65 per cent). If the heating was continued till the mixture was nearly a complete melt, the yield was reduced to a quarter and diphenylurea was the chief by-product.

Benzoyl-*p*-tolylurea and benzoyl-*p*-anisidylurea were prepared analogously in excellent yields without by-products, both crystallising from amyl alcohol, m. p. 228-29° and 219° respectively. (Found: N, 11·25. $C_{15}H_{14}O_2N_2$ requires N, 11·02 per cent. Found: N,10·68; $C_{15}H_{14}O_3N_3$ requires N, 10·37 per cent).

My best thanks are due to Prof. A. S. Khan M. A., I. E. S., for giving me facilities to carry out this work and to Dr. R. C. Ray, D. Sc., for kindly allowing me to work in his Inorganic laboratory.

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Oxidation of Sulphydril Bodies by Hydrogen Peroxide at Room Temperatures in Presence of Inorganic Catalysts. Part I. The Oxidation of Cystine and Dithioglycollic Acid in Presence of Tungstic Acid and Molybdic Acid Sols.

By J. C. Ghosh and B. C. Kar.

The discovery of glutathione by Hopkins (*Biochem. J.*, 1921, **15**, 286) has created a new interest in the study of the oxidation-reduction mechanism of sulphydril bodies. Ghosh, Roy Chaudhuri and Ganguli (*J. Indian Chem. Soc.*, 1932, **9**, 43) have shown that in neutral and alkaline medium, a reversible thermodynamic potential is established provided the dithio compound is reduced cathodically at a mercury surface and traces of oxygen are completely eliminated. This observation of Ghosh and co-workers has been confirmed by Brdicka (*Collection*, 1933, **5**, 148) by polarographic studies with dropping mercury cathode and Green (*Biochem. J.*, 1933, **27**, 678) working in Hopkin's laboratory.

Shinohara (*J. Biol. Chem.*, 1932, **96**, 285) considers that a knowledge of the oxidation mechanism of the sulphydril group to its final stage is essential to an understanding of its biological significance. He studied the oxidation of cystine by iodine and found cysteic acid as the end-product. Warburg (*Biochem. Z.*, 1921, **113**, 257) has shown that cystine is oxidised to sulphuric acid, ammonia and carbon dioxide by oxygen with specially prepared charcoal as catalyst. Dakin has carried out a large number of oxidation of substances having biochemical significance by H_2O_2 and has found that the results simulate those observed in *vivo*. Smedley-Maclean and Pearce (*Biochem. J.*, 1931, **25**, 1252) have similarly carried out the oxidation of oleic acid, by means of hydrogen peroxide. These experiments were all carried out at temperatures above 60°, whereas the life processes occur mostly at temperatures below 40°. We have found that deep seated

oxidation of sulphydril bodies by hydrogen peroxide easily takes place at temperatures between 10° to 35° provided suitable catalysts are present. The present paper deals with colloidal sols of tungstic acid and molybdic acid whose behaviour as oxidising catalysts agree in many ways with those of peroxidases.

Oxidation of Cystine by means of Hydrogen Peroxide in presence of Tungstic Acid Sol.

Procedure.—Chemically pure samples of cystine and sodium tungstate were taken, the former dissolved in hydrochloric acid (Merck's extra pure) solution and the latter in water. In all the experiments we have used the so-called conductivity water. The experiments were carried out in pyrex conical flasks which were thoroughly cleansed with 20% hydrochloric acid and finally with water. The sol was prepared five to six minutes before the actual experiment was begun by the addition of dilute hydrochloric acid to sodium tungstate solution which reacts with hydrochloric acid to form a sol according to the equation

$$4\,Na_2Wo_4+6\,HCl = Na_2O,\ 4\,Wo_3+6\,NaCl+3\,H_2O.$$

Merck's chemically pure perhydrol was used for preparing each day a fresh solution of hydrogen peroxide. The reaction mixtures were quite stable and no visible turbidity was produced. Three similar flasks, the first containing hydrogen peroxide and sol, the second cystine, hydrogen peroxide and sol, but all having the same p_H and same volume, were kept at constant temperature in a thermostat within $\pm 0{\cdot}1°$ of the required temperature. The first flask indicated that no appreciable amount of hydrogen peroxide was lost due to the spontaneous decomposition of hydrogen peroxide in the presence of the sol, under the prevailing usual experimental conditions, the second showed the absence of any decomposition of hydrogen peroxide and any reaction without the sol. From the third 0·504 c.c. aliquots were withdrawn at suitable intervals by means of a micropipette and hydrogen peroxide left over was determined by Kingzett's method,[1] 0·01*N* sodium thiosulphate being used as the titre. The amount of reaction that takes place between the unoxidised cystine and I_2 during the period of titration covering from 5 to 6 minutes is too small to affect the results. Almost all

the experiments were duplicated under conditions as strictly comparable as possible and the same results were obtained.

End products and order of the reaction.—Cysteic acid has been isolated as the main product of oxidation. Ammonia and sulphuric acid in small quantities have also been detected. Cysteic acid is produced according to the following equation,

$$R-S-S-R+5\,H_2O_2 = 2RSO_3H+4H_2O \qquad \ldots \quad (1)$$

where R represents $\text{-}CH_2{\cdot}CHNH_2{\cdot}COOH$.

The presence of small quantities of inorganic sulphate and ammonia leads us to assume that the reaction proceeds to some extent beyond the cysteic acid stage according to the following equation,

$$HSO_3{\cdot}CH_2{\cdot}CHNH_2{\cdot}COOH+H_2O_2=CH_3{\cdot}CO{\cdot}COOH+NH_3+H_2SO_4 \quad \ldots \quad (2)$$

pyruvic acid being converted into acetic acid and carbon dioxide in presence of excess hydrogen peroxide. We have actually found that ammonia is produced not in the cysteic acid stage of the reaction but at a much later stage.

In order to find out the order of the reaction which was followed till 60% conversion of cystine, we have only taken into account the oxidation of one molecule of cystine by five molecules of hydrogen peroxide, *i.e.*, reaction (1). We have found that our data in each individual experiment fit into the general equation of the first order,

$$K = \frac{1}{t_2-t_1}\log\frac{(a-x_1)}{(a-x_2)}$$

where $(a-x_1)$ is the concentration of cystine in molarity corresponding to the time " t_1 " which is generally 4 minutes after starting the reaction, $(a-x_2)$ is the concentration at any time t_2 (in minutes). Concentration of cystine at any time was found from the amount of hydrogen peroxide that disappeared at that time. It is noteworthy, however, that though in each reaction a good unimolecular velocity constant with respect to cystine was obtained, the value of this constant differed for different initial concentrations of cystine,

TABLE I.

Effect of varying the concentration of cystine.

Temp. = 21°. pH, 1·18. Conc. of Na- tungstate = 0·0005*M*.

Initial conc. of cystine.	Conc. of H_2O_2.	Reaction range selected.	* *K* (Pseudo 1st order) Limits.	Mean.
0·00417*M*	0·0878*M*	(7—60) %	0·0034—0·0031	0·0033
0·00834	0·0898	(7—50)	0·0021—0·0020	0·0021
0·01251	0·0806	(6—62)	0·0019—0·0016	0·0017

When $1/K$ against conc. of cystine is plotted graphically, a straight line is obtained (*cf.* Fig. 1).

TABLE II.

Effect of varying the concentration of hydrogen peroxide.

Temp. = 21°. pH, 1·18. Conc. of Na- tungstate = 0·0005*M*.
Conc. of cystine = 0·00417*M*.

Initial conc. of H_2O_2	...	0·0247	0·0408	0·0878
K	...	0·0015	0·0021	0·0033

When $1/K$ against $1/$conc. of H_2O_2 is plotted graphically, a straight line is obtained (*cf.* Fig. 2.).

FIG. 1.

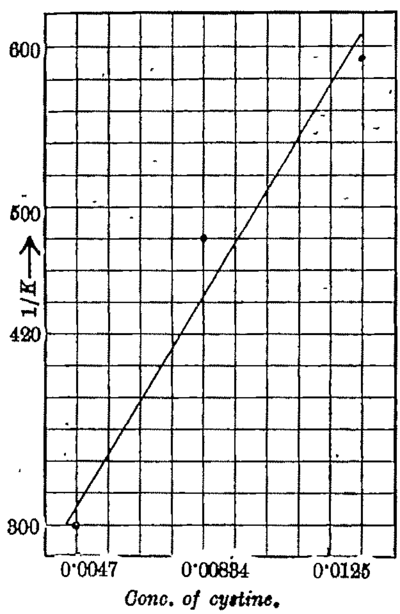
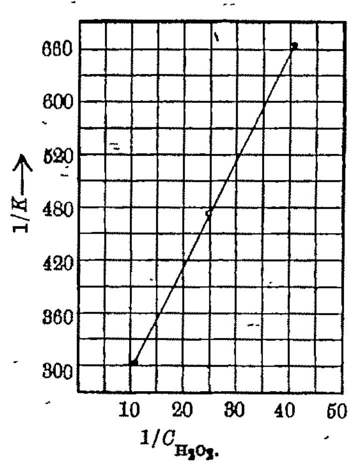


FIG. 2.



* In all the experiments following we have given only the mean value of the constants obtained between the same reaction range.

TABLE III.

Effect of varying the concentration of sodium tungstate.

Temp. = 21°. p_H, 1·13. Conc. of cystine = ·00417M.

Conc. of H_2O_2.	Conc. of Na- tungstate.	K.
0·0455 M	0·0005 M	0·0023
0·0467	0·001	0 0034
0·0461	0·002	0·0055

TABLE IV.

Effect of varying the p_H.

Temp. = 31°. Conc. of cystine = 0·00417M. Conc. of Na-tungstate = 0·0005M.

Conc. H_2O_2 (M)	... 0·0235	0·0246	0·0246	0·0254	0·0260	0·02578
p_H	... 0·92	1·13	1·77	2·5	3·5	5·0
K	... 0·0033	0·0035	0·0025	0·0018	0·0028	0·0048

The p_H of the reaction mixtures was gradually increased by the addition of requisite amount of distilled ammonia. Since the product of the reaction is acidic we used at the higher p_H 3·5 and 5, acetate buffers at suitable concentrations so that it did not cause any spontaneous decomposition of hydrogen peroxide.

TABLE V.

Effect of varying the temperature.

p_H, 1·13. Conc. of cystine = 0·00417M. Conc. of Na-tungstate = 0·0005M.

Temp.	Conc. of H_2O_2.	K.
11°	0·025 M	0·0008
21	0·0247	0·0015
31	0·0246	0·0035

Influence of traces of salts.—The oxidation of cystine by means of hydrogen peroxide does not take place in presence of the following salts, *viz.*, $CuSO_4$, $5H_2O$; $FeSO_4$, $7H_2O$; $MnCl_2$, $4H_2O$; $Cr_2(SO_4)_3$, $18H_2O$; $Ce_2(SO_4)_3$; KCN. But most of them promote the activity of the tungstic acid sol as shown in Table VI.

TABLE VI.

Temp.=21°. pH, 1·18. Conc. of cystine=0·00417*M*. Conc. of Na_2WO_4=0·0005 *M*.

Salts.	Conc.	Conc. of H_2O_2.	*K*.
—	—	0·247 *M*	0·0015
$FeSO_4$, $7H_2O$	$4{\cdot}07\times10^{-4}M$	0·0248	0·0022
$CuSO_4$, $5H_2O$	$4{\cdot}26\times10^{-5}$	0·0238	0·0022
$MnCl_2$, $4H_2O$	$4{\cdot}05\times10^{-4}$	0·0239	0·0018
$Cr_2(SO_4)_3$, $18H_2O$	4×10^{-4}	0·0239	0·0020
$Ce_2(SO_4)_3$	4×10^{-4}	0·0245	0·0018
KCN	$1{\cdot}04\times10^{-3}$	0·0247	0·0015

Oxidation of Cystine by means of Hydrogen Peroxide in presence of Molybdic Acid Sol.

Procedure.—Here the experimental procedure is exactly the same as in the case of tungstic acid sol. A sample of ammonium molybdate having the molecular formula $(NH_4)_6$, Mo_7O_{24}, $4H_2O$ was taken. In actual experiments its molecular weight was taken to be equal to one seventh of its true molecular weight corresponding to one atom of molybdenum. The sol was prepared 5 to 6 minutes before the experiment by the addition of HCl to ammonium molybdate, the strength of the former in normality being double the strength of the latter in molarity.

TABLE VII.

Effect of varying the concentration of cystine.

Temp.=31°. pH, 1·18. Conc. of Am. molybdate=0·0005 *M*.

Initial conc. of cystine.	Conc. of H_2O_2.	*K* (unimol. velocity constant with respect to cystine).
0·00417 *M*	0·07 *M*	0·00290
0·00834	0·0693	0·00246
0·01251	0·0693	0·00209

The graph of $1/K$ against concentration of cystine is a straight line (*cf.* Fig. 3).

TABLE VIII.

Effect of varying the concentration of hydrogen peroxide.

Temp. = 31°. p_H, 1·18. Conc. of Am. molybdate = 0·0005M. Conc. of cystine = 0·00417M.

Initial conc. of H_2O_2 (M)	...	0·0284	0·0388	0·07
K	...	0·00183	0 00235	0·00290

When $1/K$ against 1/conc. of hydrogen peroxide is plotted graphically, a straight line is obtained (*cf.* Fig. 4).

FIG. 3.

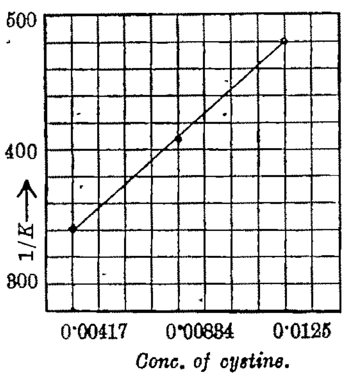


FIG. 4.

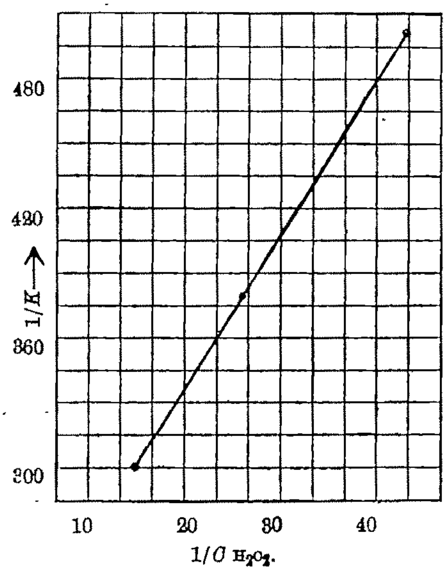


TABLE IX.

Effect of varying the concentration of ammonium molybdate.

Temp. = 31°. p_H, 1·77. Conc. of cystine = 0·00417 M.

Conc. of H_2O_2.	Conc of Am. molybdate.	K.
0·0235 M	0·00025 M	0·0018
0·0229	0·0005	0·00324
0·0235	0·001	0·0061

TABLE X.

Effect of varying the p_H.

Temp. = 31°. Conc. of cystine = 0 00417*M*. Conc. of Am. molybdate = 0·0005*M*.

Conc. of H_2O_2 (*M*) ...	0·0233	0·0234	0·0229	0·0252	0·0258	0·0258
p_H ...	0·92	1·13	1·77	2·5	3·5	5·0
K ...	0·00155	0·00183	0·00324	0·0059	0·0089	0·0115

TABLE XI.

Effect of varying the temperature.

Conc. of cystine = 0·00417*M*. Conc. of Am. molybdate = 0·0005*M*.

Temp.	Conc. of H_2O_2.	p_H.	*K*.
21°	0·0234 *M*	1·13	0·0009
31	0·0234	1·13	0·00183
21	0·0235	1·77	0·0015
31	0·0230	1·77	0·00324

Oxidation of Dithioglycollic Acid by Hydrogen Peroxide in presence of Tungstic Acid Sol.

The oxidation of dithioglycollic acid takes place in exactly the same manner as that of cystine. The sulphydril compound is first rapidly converted into its disulphide form in presence of the sol and the dithioglycollic acid is slowly oxidised to sulphoacetic acid as cystine is oxidised to cysteic acid in accordance with the following stoichiometrical equations,

$2\,R-SH+H_2O_2=R-S-S-R+H_2O$ (rapid reaction)
$R-S-S-R+5\,H_2O_2=2RSO_3H+4H_2O$ (slow reaction)
R representing $-CH_2\cdot COOH$.

Procedure.—The experimental procedure is similar to that in the case of cystine. The thioglycollic acid solution was freshly prepared everyday. Three pyrex conical flasks, one containing sol and hydrogen peroxide, the second thioglycollic acid and hydrogen peroxide

were taken all having same p_H and same volume. The first did not show any perceptible decomposition of hydrogen peroxide. In the second flask the thioglycollic acid was slowly converted into dithioglycollic acid as determined by an alcoholic iodine solution. In the third vessel the first reaction was very quick and the velocity of the second reaction was measured after the first reaction was over. The amount of hydrogen peroxide left was determined by Kingzett's method.

The velocity was represented by a unimolicular equation of the form, $K=\frac{1}{t_2-t_1}\log\frac{(a-x_1)}{(a-x_2)}$.

TABLE XII.

Effect of varying the concentration of thioglycollic acid.

Temp. $=21°$. pH, 2·2. Conc. of $Na_2WO_4=0·001M$.

Initial conc. of thioglycollic acid.	Conc. of H_2O_2.	K.
0·00776 M	0·0877M	0·0021
0·01552	0·0891	0·0018
0·0221	0·0865	0·0017

TABLE XIII.

Effect of varying the concentration of hydrogen peroxide.

Temp. $=21°$. pH, 2·2. Conc. of Na-tungstate $=0·001M$.

Conc. of thioglycollic acid.	Initial conc. of H_2O_2.	K.
0·0079M	0·0238M	0·0016
0·0079	0·0462	0·0018
0·0078	0·0877	0·0021

TABLE XIV.

Effect of varying the concentration of sodium tungstate.

Temp. $=21°$. pH, 2·2.

Conc. of thioglycollic acid.	Conc. of H_2O_2.	Conc. of Na-tungstate.	K.
0·0078M	0·0452M	0·0005M	0·0011
0·0079	0·0462	0·001	0·0018
0·0079	0·0442	0·002	0·0030

TABLE XV.

Temp. $=21°$. pH, 1·62.

Conc. of thioglycollic acid.	Conc. of H_2O_2.	Conc. of Na-tungstate.	K.
0·00797M	0·0458M	0·00025M	0·0013
0·00785	0·0456	0·0005	0·0019
0·0078	0·0448	0·001	0·0033
0·0079	0·0461	0·002	0·0060

TABLE XVI.

Effect of varying the p_H.

Temp. = 21°. Conc. of Na-tungstate = 0·0005*M*.

Conc. of thioglycollic acid (*M*) ...	0·00790	0·00785	0·00777	0·00782	0·00793	0·00775	0·00775
Conc. of H_2O_2 (*M*)	0·0455	0·0456	0·0451	0·0452	0·0445	0·0474	0·0471
pH	1·35	1·62	1·93	2·2	2·4	3·9	5·4
K	0·00176	0·0019	0·00156	0·0011	0·00095	0·0019	0·0035

TABLE XVII.

Effect of varying the temperature.

pH, 2·2. Conc. of Na-tungstate = 0·0005*M*.

Temp.	Conc. of thioglycollic acid.	Conc. of H_2O_2.	*K*.
11°	0·0078*M*	0·0465*M*	0·00047
21	0·0078	0·0452	0·0011
31	0·00786	0·0485	0·0027

DISCUSSION

The oxidation of cystine and dithioglycollic acid by hydrogen peroxide to form respectively cysteic acid and sulphoacetic acid has the following characteristic features:

(1) In presence of tungstic acid sol and molybdic acid sol as catalysts, the reaction takes place quickly at room temperature.

(2) The progress of the reaction in any particular experiment with a definite initial concentration of cystine or dithioglycollic acid can be represented with considerable accuracy by a unimolecular equation provided hydrogen peroxide is present in excess. But unlike the case of true unimolecular reactions, the unimolecular constant is not independent of the initial concentration of the reductant but diminishes as the initial concentration of the reductant increases.

(3) The unimolecular velocity constant increases as the initial concentration of hydrogen peroxide increases.

(4) In the case of the molybdic acid sol as catalyst, the velocity concentration continually increases as the p_H of the medium increases from 1 to 5. Beyond p_H 5, hydrogen peroxide undergoes slow spontaneous decomposition and therefore the optimum condition could not be determined.

(5) In the case of the tungstic acid sol as catalyst, the velocity constant between p_H 1—2·5 has an optimum value at p_H 1·18 for cystine and at p_H 1·62 for dithioglycollic acid. But as the p_H is increased from 2·5 to 3·5 the velocity constant again increases and continues to increase up to p_H 5. Beyond this hydrogen peroxide undergoes perceptible spontaneous decomposition and therefore the second optimum p_H could not be determined.

(6) For each 10° rise in temperature the velocity constants increase about 2—2·3 times.

(7) The following salts [$CuSO_4$, $5H_2O$; $FeSO_4$, $7H_2O$; $MnCl_2$, $4H_2O$; $Cr_2(SO_4)_3$, $18H_2O$; $Ce_2(SO_4)_3$] in very low concentrations do not decompose hydrogen peroxide but they promote the catalytic activity of tungstic acid sol.

(8) Potassium cyanide has no influence on the catalytic activity of the sol indicating that the sol as such and not impurities like iron salts present in traces in the sol, is the active catalytic agent.

(9) As the stoichiometric concentration of the sol is increased, the velocity constant of the reaction increases but not in exact proportion to the increase in the concentration of the sol. This indicates that the active surface of the sol, does not increase in proportion to its increase of stoichiometric concentration. The particle size increases with increase in the concentration of the tungstate and molybdate used for sol formation and hence the specific surface or the ratio $\frac{\text{active surface}}{\text{mass}}$ diminishes.

The peculiarities noted in section (2) and (3) above can be explained by the following mechanism of reaction:—

The reaction only takes place between the molecules of reductant and hydrogen peroxide actually adsorbed on the surface of the sol. We assume further that for equivalent concentrations, the adsorption coefficient of cystine is the same as that of cysteic acid and that of dithioglycollic acid is the same as that of sulphoacetic acid. The portion of the sol surface covered jointly by cystine and cysteic acid or by dithioglycollic acid

and sulphoacetic acid remains, therefore, constant throughout the progress of the reaction in a particular experiment and the fraction depends only on the initial concentration of the reductant. Let a_1 be the fraction of the sol surface covered by the reductant and the oxidised product together, when the initial concentration of the reductant is c_1. Then at any time during the progress of the reaction the fraction of the surface covered by the reductant is $a_1 \dfrac{(c_1-x)}{c_1}$ and the fraction covered by the oxidation product is $\dfrac{a_1 x}{c_1}$ where x is the concentration of the reductant oxidised in time "t". If a' is the fraction of the surface area covered by molecules of hydrogen peroxide, and if the velocity of reaction is proportional to the product of the surface concentrations of the reductant and of hydrogen peroxide, then

$$\frac{dx}{dt} = K_3 . a' . a_1 \frac{c_1-x}{c_1} \qquad \ldots \qquad \ldots \qquad (i)$$

But according to Langmuir's ideas

$$a_1 = \frac{K_1 c_1}{K_2 + K_1 c_1} \quad \text{and} \quad a' = \frac{K' c'}{K'' + K' c'}$$

where c_1 is the initial concentration in solution of the reductant and c' is the concentration of hydrogen peroxide. If, as in our experiments the concentration of hydrogen peroxide is always in excess, c' may be considered to be constant throughout the course of the reaction. Hence

$$\frac{dx}{dt} = K_3 . \frac{K'c'}{K''+K'c'} . \frac{K_1 c_1}{K_2 + K_1 c_1} . \frac{c_1 - x}{c_1} \qquad \ldots \qquad (ii)$$

$$\text{or} \quad K_3 . \frac{K'c'}{K''+K'c'} . \frac{K_1}{K_2+K_1 c_1} = \frac{1}{t} \log \frac{c_1}{c_1 - x} = K \text{ (Experimental value as given in tables)} \qquad \ldots \qquad (iii)$$

If c', *i.e.*, the concentration of hydrogen peroxide is in excess the experimental value of the unimolecular velocity constant K will depend on the value of c_1, the initial concentration of the reductant. K will diminish as c_1 increases, and it follows from (*iii*) that $1/K$

plotted against c_1 will be a straight line. This has been verified (*cf.* Figs. 1 and 3).

Again for the same initial concentration of reductant c_1, the value of the unimolecular constant K will depend on the value of c, the concentration of hydrogen peroxide. In fact, unlike the previous case, the value of K will increase as the concentration of hydrogen peroxide increases. According to Equation (*iii*)

$$\frac{1}{K}=\frac{1}{K_3}\left[\frac{K_2+K_1c_1}{K_1}\right]\left[\frac{K''}{K'c'}+1\right]$$

i.e., for constant value of c_1, the reciprocal of the observed velocity constant plotted against the reciprocal of the concentration of hydrogen peroxide will be a straight line. This has also been verified (*vide* Figures 2 and 4).

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Parachor and Ring Structure. Part I.

By Susil Kumur Ray.

The parachor's contribution of ring compounds has been investigated by Sugden and his co-workers, and the parachor values of the 3-, 4-, 5-, and 6-membered rings have been determined by them. Sugden in his investigations considered generally the homocyclic carbon compounds with the object of finding the influence of the number of atoms in a ring system on its parachor value. The present investigation is undertaken to decide whether there is any specific influence of a ring structure on the parachor values, or whether the number of atoms (and their mode of linkage) is the only factor to be taken into consideration.

In the present paper, data are given for fifteen cyclic compounds. The surface tension has been determined by the method of maximum bubble pressure. The apparatus employed was of the usual Sugden type. Tubes containing activated charcoal were introduced between the bubbler and the manometer to prevent the fouling of the alcohol surface by the vapour of the liquid in the bubbler, as in the work of Hammick and Andrew (*J. Chem. Soc.*, 1929, 754). The specific gravity of the liquids were determined with a 10 c. c. specific gravity bottle, while that of the solids by means of a U-shaped pyknometer as employed by Sugden. Pressure differences were read correct to 0·05 mm. and the error is probably not more than $\pm$0·02 mm. The surface tension and the density determinations were made at the same temperature ($\pm$0·50). The bubblers were standardised with benzene (M.R.), purified by crystallisation and then distillation, and were restandardised before each observation.

The liquids and the solids used were very carefully purfied, the former by distillation, generally under reduced pressure and the latter by repeated crystallisation until there is no change in the surface tension or density.

The observed values of the parachor for these substances are given in the fourth column of the following tables; the column headed $\Sigma[P]$ gives the sum of the atomic and structural constants except that for the ring, so that the effect of this structure if obtained by subtracting $\Sigma[P]$ from $[P]_{obs}$ and is given in the last column.

TABLE I.

Pyridine and condensed benzopyridine rings.

	Temp.	Density.	Surface tension.	$[P]_{obs.}$	$\Sigma[P]$.	Diff.theor.	Diff.obs.
Pyridine	25·5°	0·9890	37·52	197·4	191·6	6·1	5·8
Piperidine	27·0°	0·8980	34·87	230·0	224·6	6·1	5·
a-Picoline	26·0°	0·9559	34·74	236·3	230·6	6·1	5·
Quinoline	26·0°	1·098	44·61	303·6	291·4	12·2	12·2
Quinaldine	27·5°	1·053	40·72	343·1	330·3	12·2	12·8
8 Oxyquinoline	98·5°	1·127	39·68	322·8	311·4	12·2	11·4
*iso*Quinoline	26·8°	1·108	46·28	303·8	291·4	12·2	12·4

It is evident from Table I that the parachor value of the pyridine ring is about the same as that of benzene nucleus. Hence the substitution of a carbon atom in benzene by a nitrogen atom has no effect on the parachor. Moreover, by the fusion of two ring systems as in quinoline and its derivatives, the parachor value of the separate nuclei remains unaltered. This observation is also supported by the work on naphthalene derivatives (Vogel, *J. Chem. Soc.*, 1928, 2017; Bhatnagar and Singh, *J. Indian Chem. Soc.*, 1929, **6**,263).

TABLE II.

Five membered ring system.

	Temp.	Density.	Surface tension.	$[P]_{obs.}$	$\Sigma[P]$.	Diff.theor.	Diff.obs.
*cyclo*Pentanone	29·0°	0·9485	32·33	212·3	204·0	8·5	8·3
Furfuraldehyde	30·0°	1·152	41·09	210·1	202·0	8·5	8·1
Pyrrole	29·0°	0·9809	28·80	166·7	163·6	8·5	3·1
Succinimide	126°	1·242	45·20	206·7	208·6	8·5	8·1
Nicotine	31·2°	1·005	36·50	396·3	382 0	14 6	14·3
Indene	30·5°	1·004	36·99	284·9	272·8	14·6	12·1
Phthalic anhydride	130°	1·238	39·50	295·1	282·8	14·6	12·3
Indole	99·5°	1·070	37·39	270·2	263·4	14·6	6·8

It will be seen that the substitution of a carbon atom in *cyclo*pentane derivatives by an oxygen atom has no effect on the parachor contribution; but the replacement by a nitrogen atom as in pyrrole, succinimide and indole, reduces the parachor value by about 5·5 units. In nicotine, where the pyrrole ring is fully saturated, the normal value is found. It thus appears that not only the nature of the substituents but the degreee of unsaturation of atoms in forming a ring as well, influences the parachor to a certain extent. It is also of interest to note that though the condensation of two six membered rings has no effect on the parachor, the condensation of a six and a five membered ring, as in indene, phthallic anhydride and indole, lowers the parachor by about 2·5 units.

It is obvious, therefore, that in this series as in other (*cf.* Sugden and co-workers, *J. Chem. Soc.*, 1925, 1868; 1927, 189) the parachor is not strictly an additive function of atomic structural constants, but that these constants vary slightly from substance to substance. The variation in the constant for the five membered ring appears to be in harmony with modern views as to the effects of substituents on the stability of rings. The effect of various other types of ring structures on the parachor contribution is under investigation.

My grateful thanks are due to Prof. P. R. Rây of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest they took in the work.

Chemical Laboratory.,
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Received March 19, 1934.

Obituary

PROFESSOR ANDREW NORMAND MELDRUM

Born 19th March, 1876. Died 12th March, 1934.

By the unexpected death of Professor Andrew Normand Meldrum on March 12th, the Indian Chemical Society has lost one of its Foundation Fellows. He took a keen interest in the activities and progress of the Society. He was (Honorary) Editor from 1925-26 and its Vice-President from 1927-29. He took great interest in starting the Bombay Section of the Society and was its President for about three years.

Professor Meldrum was born on March 19th 1876 in Scotland and was educated first at the Royal College of Science, London and then at Aberdeen University and at the Victoria University, Manchester. Between 1899 and 1901 he published with Japp papers on the interaction of phenanthraquinone, acetophenone and ammonia, on the condensation of benzoin and phenols, and on the homologues of anhydracetonebenzil which cleared some doubtful points regarding their constitution. Professor Meldrum next appears to devote his attention to the atomic theory. In 1904 he was awarded the D.Sc. degree by the University of Aberdeen on a Thesis on "Avogadro and Dalton: The standing in Chemistry of their hypotheses" which was published in the same year. He was awarded a Research Fellowship from the Carnegie Trust and started work with Turner at Sheffield on the "Complexity of amides in various solvents." He appears to have carried out a part of this work in Perkin's laboratory at Manchester where he also obtained one of the two known stable β-lactones by the interaction of acetone and malonic acid in the presence of acetic anhydride and sulphuric acid. In 1911 he published a paper on substances related to cochenillic and carminic acids. He synthesised the methyl ether of β-coccinic acid and found it to be identical with that obtained by the degradation of cochenillic acid, the colouring matter of cochineal.

In 1912 he joined the Indian Educational Service and was appointed Professor of Chemistry at the M. R. Institute of the

Gujerat College, Ahmedabad. In 1920 he took up work on "Derivatives of gallic acid," and also published a brochure on "The development of the atomic theory" in continuation of his earlier work. In 1922 he was transferred to the Royal Institute of Science, Bombay, where he proved a most successful teacher and administrator, and carried out most of his research work in India. He was interested in the chloral condensations. One of his students the late Mr. K. S. Vaidyanathan synthesised cochenillic acid under his guidance. A new synthesis of indigo was also achieved by him as a result of the study of certain chloral condensations. Another important result of his study of chloral condensations is the discovery of a new method for the synthesis of substituted phenylacetic acids. On the inorganic and physical side he worked with his students on the isolation of boric acid complexes with polyhydroxy substances and also on the study of certain physical properties of solutions of sodium borate. Administrative duties as Principal of the Royal Institute of Science did not leave him much time. He published about nine papers in the Journal of the Indian Chemical Society. Two of his papprs in collaboration with students are still awaiting publication in the same Journal.

Towords the end of his career in India Professor Meldrum again took up his researches in historical chemistry in right earnest. He published a monograph on "The Eighteenth Century Revolution in Science: First Phase" in 1931 and in this as well as in various papers on this subject he showed himself, as has been remarked in Nature (May 19, 1934) "a close student as well as a keen and at times, outspoken critic." In April 1933 he read before the Chemical Society, London, three addresses on Joseph Priestley on the occasion of the Bicentenary Celebrations of that philosopher.

While in India Professor Meldrum took an adequate interest in various scientific and educational activities. He was President of the Chemistry Section of the Indian Science Congress in 1923. He was a member of the Senate, on the Syndicate and was elected (in 1930) Dean of the Faculty of Science of the Bombay University. He took a prominent part as a member of the Visvesvaraya committee appointed by the University of Bombay for drafting a scheme for starting the department of Chemical Technology. He was nominated as a trustee of the Prince of Wales Museum and as a member of the Provincial Council of Agricultural Research.

He retired from service in India in 1931 and went to his home in Edinburgh to spend the remainder of his life. During the short

period of his retirement he continued to be busy with historical chemistry and before his death he was actively engaged in a careful scrutiny of the contemporary and subsequent literature relating to Black's discoveries.

His only son died in 1933. This appears to have had its effect on him. He then decided to move to Berkshire but died while completing the final preparations for moving. He leaves behind him a widow and two daughters.

He undertook cheerfully the onerous duties of a Honorary Editor (Organic section) of the Journal of the Society. He was most polite in meeting the criticisms of authors against the decisions of the Editor and we recall with pleasure his attitude in these matters. He was for maintaining a proper standard but at the same time believed in polite persuasion. He gave the Society his wholehearted support. One of us had the pleasure of meeting him in 1932 at his home and the hospitality he enjoyed from both Prof. and Mrs. Meldrum on that occasion and the eager interest with which he discussed the various problems relating to our Society will ever remain as a pleasant remembrance of his genial personality.

Below is given an account of various papers published by Prof. Meldrum himself and with his collaborators.

Substances related to cochenillic acid and carminic acids. Part I. Synthesis of the methyl ether of β- and of α- coccinic acid. (*J. Chem. Soc.*, 1911, **99**, 1712).

The development of atomic theory. Part II. The various accounts of the origin of Dalton's theory. (*Mem. Manchester Phil., Soc.*, 1911, **55**, No.3).

Part III. Newton's theory and its influence in the eighteenth century. (*ibid.*, **55**, 1911, No. 4). Parts IV-VI. (*ibid.*, 1911, **55**, No. 6, No. 19). Part VII. (*ibid.*, 1912, **56**, No. 22).

With R. L. Alimchandadni—Derivatives of gallic acid. Part II. (and the cresotic acids) and chloral. (*J. Chem. Soc.*, 1921, **119**, 20).

The reduction of the group $-CH(OH)\,CCl_3$. Part I. (*J. Indian Chem. Soc.*, 1925, **2**, 1).

Substances related to cochenillic and carminic acids. Part II. Synthesis of α- coccinic acid (*m*- oxyuvitic acid). (*ibid.*, 1929, **6**, 253).

With N. W. Hirve—Derivatives of salicylic acid. Part II. 3-Nitro-5-sulpho- and 5-nitro-3-sulphosalicylic acids. (*ibid.*, 1930, **7**, 887).

Derivatives of salicylic acid. Part I. (*ibid.*, 1928, **5**, 95).

With M. M. Patel—The sodium and potassium phenolates. (*ibid.*, 1928, **5**, 91).

With M. S. Shah—A synthesis of 5-hydroxy-2-methoxybenzoic acid. (*ibid.*, 1931, **8**, 575).

With B. M. Kapadia—Condensation of chloral with 2-hydroxy-*p*-toluic acid and its methyl ester. (*ibid.*, 1932, **9**, 483).

With Miss B. N. Katrak—Condensation of butylchloral with gallic acid and three cresotic acids. (*ibid.*, 1932, **9**, 121).

With A. H. Advani—The condensation of methyl and ethyl-*o*-toluidines with chloral hydrate. (*ibid.*, 1933, **10**, 107).

With W. E. S. Turner—Molecular complexity of amides in various solvents. Parts I, II, and III. (*J. Chem. Soc.*, 1908, **93**, 876, 1910, **97**, 1605, 1805).

With W. A. Perkin (jun)—The reduction of 5-hydroxy-*m*-toluic acid. (*J. Chem. Soc.*, 1909, **95**, 1889).

The *cis* and *trans* modification of 1-methyl*cyclo*hexane-2-ol-4-carboxylic acid. (*ibid.*, 1908, **93**, 1416).

With Francis R. Japp—Interaction of phenanthraquinone, acetophenone, and ammonia. (*J. Chem. Soc*, 1899, 75, 1032.)

Furfuran derivatives from benzoin and phenols. (*ibid.*, 1899, **75**, 1035).

Interaction of benzoin with phenylenediamines. (*ibid.*, 1899, **75**, 1043).

Homologues of anhydracetonebenzil. (*ibid.*, 1901, **79**, 1024).

J. N. M.

S. M. M.

The Concept of Critical Increment and Radiation Hypothesis.

BY W. V. BHAGWAT.

It is well known that the variation of velocity constant of chemical reaction with temperature is given by the relation

$$\frac{d\log k}{dT}=\frac{E}{RT^2}$$

where E is the so-called critical increment in energy which activates a molecule.

The radiation hypothesis for explaining this equation proceeds from the Planck equation,

$$\frac{\text{Probability of no emission by oscillator}}{\text{Probability of emission by oscillator}}=1/e^{\frac{h\nu}{kt}}-1$$

and assumes that this expression also gives the ratio

$$\frac{\text{No. of active molecules}}{\text{No. of inactive molecules}}.$$

$$\text{Hence, }\frac{\text{No. of active molecules}}{\text{Total No. of molecules}}=e^{-h\nu/kT}=e^{-Nh\nu/RT}$$

if E is identified with $Nh\nu$.

The term E, represents critical increment, before a molecule becomes active. It is possible to conceive that a molecule retains its absorbed energy, but the energy is not sufficient to bring it to critical state. In this case we cannot identify the active state with the state of energy retention. Secondly, a molecule may lose its energy that has been absorbed, and still possess an energy greater than the critical. In this case again we fail to identify the two states of energy emission and inactive condition. It will be clear, therefore, that the above assumption introduced in deducing $E=Nh\nu$ is doubtful. Really the equation

$$\frac{d\log k}{dt}=\frac{Nh\nu}{RT^2}$$

does not represent the variation of the velocity constant with temperature, and k, is not really the velocity constant of the chemical reaction, but represents the variation in the number of molecules which are capable of retaining the absorbed energy of the frequency ν, with temperature. It follows, therefore, that this k is not necessarily identical with the k of Marcelin and Rice's equation which corresponds to velocity constant of the reaction and hence we are not justified in putting $R=Nh\nu$.

Consequences of our failure in identifying the active and energy retention state are obvious. Since $E \neq Nh\nu$

(1) The ν, so calculated on the basis of identity between two states need not be absorbed by the reacting system.

(2) The radiation may be absorbed but it fails to accelerate the reaction, since the process of energy retention need not necessarily increase the energy to critical state.

These conclusions are in accordance with the experimental observations. We find that the Radiation hypothesis fails in two ways:

(*i*) The calculated wave-length from $E=Nh\nu$ is not absorbed by the reacting system.

(*ii*) The absorbed wave-length fails to accelerate the reaction.

These two ways of failure are identical according to my conclusion. It is clear, therefore, that this deviation is mainly due to the reason mentioned above.

Thus according to Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 53) there is no acceleration of the reaction for nitrogen pentoxide by the radiation of wave-length 11600 Å which is obtained from temperature coefficient. Similar results were obtained by Daniels (*ibid.*, 1927, **49**, 617) in case of N_2O_5 ; by Urey and Tolman (*ibid.*, 1929, **51**, 974) for the velocity of recemisation of *d*-pinene in liquid state ; by Fromageot (*Bull. Soc. chim.*, 1927, *iv*, **41**, 1585) in the reduction of ceric salts by acetaldehyde and by Hibben (*Proc. Nat. Acad. Sci.*, 1927, **13**, 626 ; *J. Amer. Chem Soc.*, 1928, **50**, 937, 940) for the decomposition of nitrous oxide when exposed to infra-red radiations. All these deviations, therefore, can be explained from view point of the present author.

However, when there is identity between active state and the state of energy retention for a molecule, then $E=Nh\nu$ and hence the value of ν calculated from temperature coefficient should be absorbed by the reacting system and should accelerate the reaction. The experiments which confirm the radiation hypothesis

can be explained in this way. The observations of Lewis and Taylor (*J. Chem. Soc.*, 1922, **121**, 665) in case of decomposition of triethyl sulphonium bromide in various solvents, of Moran and Lewis (*J. Amer. Chem. Soc.*, 1922, **44**, 2286), for cane sugar inversion which support the radiation hypothesis, are characteristic reactions in which the active state and energy retention state are identical.

The author's conclusions are also interesting in the sense, that it gives a physical significance to the important modification of radiation hypothesis, by Dhar ("Chemical action of Light," 1931, p. 334; Gopal Rao and Dhar, *J. Phys. Chem.*, 1932, **36**, 646) that the frequency ν calculated from the temperature coefficient should be regarded as 'threshold frequency"; that is the minimum frequency that can accelerate the reaction. Dhar gives no sound justification for this statement. It may now be pointed out that the identity between active state and the energy retention state of Planck, is a limiting case by itself, or in the limit $E=Nh\nu$ and hence the frequency ν, so obtained denotes the threshold frequency which can start the chemical change, provided the two states are identified. Thus Dhar's view follows as a necessary consequence.

My best thanks are due to Prof. N. R. Dhar for his kind interest in this paper.

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A Note on the Benzoin-Benzil Change.

By K. Madhusudanan Pandalai.

It is well known that benzoin usually gives (*i*) benzoin anilide Ph·CH·(NHPh)·CO·Ph when heated with aniline, (*ii*) benzoin-anile anilide Ph·CH·(NHPh)·C·(NPh)·Ph when heated with aniline hydrochloride at 160°, and (*iii*) diphenylindole when heated with aniline and zinc chloride (*Ber.*, 1893, **26**, 1336, 2640) or when heated with aniline and aniline hydrochloride with a fractionating column (Fennel and Plant, *J. Chem. Soc.*, 1932, 2872; Japp and Murray, *ibid.*, 1894, **65**, 889).

In an attempt to prepare some 2:3-diphenylindole by the method of Fennel and Plant (*loc. cit.*) it has been found that the product obtained is contaminated by small quantities of a crystalline substance identified to be benzil. The clue obtained here of obtaining this diketone from the reaction mixture has been worked out and it has been found that by modifying Fennel and Plants' method by dispensing with the use of a fractionating column, benzoin gives with aniline hydrochloride a mixture of benzil with small quantities of diphenyl.

The mechanism of oxidation of benzoin to benzil here seems to proceed according to the following scheme and the fact that all the products formed have been identified favours this explanation.

$$\begin{array}{c} Ph\cdot CO \\ | \\ Ph\cdot CHOH \end{array} \longrightarrow \underset{\text{(Hydrobenzoin or } isobenzoin)}{\begin{array}{c} Ph\cdot C(OH) \\ \| \\ Ph\cdot C(OH) \end{array}} \xrightarrow[HCl]{2\,NH_2\cdot Ph} \begin{array}{c} C_6H_5 \\ | \\ C_6H_5 \end{array} + \begin{array}{c} Ph\cdot CO \\ | \\ Ph\cdot CO \end{array} + NH_4Cl + NH_3$$

The presence of *iso*benzoin is proved by the fact that benzoin reduces acid chlorides according to the following equation (*cf.* Klinger, *Ber.*, 1890, **24**, 1268; 1898, **31**, 1217).

$$4\,ROCl + 4H \longrightarrow \begin{array}{c} RCOH \\ | \\ RCOH \end{array} + 2ROCl \longrightarrow 2R\cdot CO\cdot CO\cdot R$$

It should be admitted that aniline and aniline hydrochloride mixture has no oxidising action on secondary alcoholic groups, as the effects observed with benzoin could not be duplicated so as to get similar α-diketones from corresponding alcohols, cuminil from cuminoin, anisil from anisoin, furil from furoin and piperil from piperoin could not be obtained. It, therefore, seems compatible to attribute this apparent anomalous action of benzoin to (*i*) its highly tautomeric nature, (*ii*) its selective reactivity to reagents, and (*iii*) its peculiar susceptibility to variations in experimental conditions.

Experimental.

Benzoin (16 g.), aniline (24 g.) and aniline hydrochloride (24 g.) were refluxed on a water-bath for 1½ to 2 hours. Ice-cold dilute hydrochloric acid was added to the yellow liquid, when a syrupy yellowish mass separated. This was filtered, washed several times with dilute hydrochloric acid and dried. On extracting this with hot alcohol repeatedly (charcoal) a dark brown oil separated and fine needles crystallised from the supernatant liquid. The supernatant liquid was decanted and again treated with animal charcoal, when benzil was obtained as bright yellowish needles, m.p. 95°, yield 12 g. The *osazone* is obtained as yellow crystals, m.p. 215°; the *semicarbazone*, m.p. 175° (benzil monosemicarbazone, m.p. 175°). That the two keto groups are adjacent in this product was proved by the fact that it was capable of condensing with *o*-phenylenediamine to give a quinoxaline derivative (Mosettig and Kamp, *J. Amer. Chem. Soc.*, 1932, **54**, 3332).

The mother liquor was now made alkaline by sodium hydroxide solution, the separated aniline removed and the solution steam distilled, when a white crystalline substance was obtained in the distillate. This was crystallised from alcohol, m.p. 71°, yield 3 g. It was identified to be diphenyl (dibromo derivative, m.p. 164°, dinitro derivative, m.p. 233°).

On keeping the brown oil mentioned above for a week, a further quantity (1 g.) of diphenyl formed on the surface of it. The oily mass could not be identified. It is soluble in hot organic solvents, *e.g.*, ether, alcohol, benzene, etc. The steam distilled solution on qualitative examination revealed the presence of the chlorides of sodium and ammonium.

Andhra University, Waltair. *Received November* 8, 1933.

Behaviour of Cobaltous Oxide on Heating.

By Mata Prasad, S. M. Mehta and T. S. Suratkar.

Hedvall (*Z. anorg. Chem.*, 1922, **121**, 217) has found that the physical and chemical properties of ferric oxide undergo a change when the oxide is prepared at different temperatures. Prasad and Tendulkar (*J. Chem. Soc.*, 1931, 1403) have also found that the physical and chemical properties of nickelous oxide change remarkably, when the temperature at which the oxide is prepared is raised. These authors have pointed out the importance of these results in the separation of nickel from the nickel-copper matte by the action of dilute sulphuric acid. This paper contains the results of a similar investigation on the properties of cobaltous oxide.

Experimental.

Kahlbaum's extra pure cobalt carbonate, free from iron and nickel, was heated for 2 hours in a silica boat under vacuum to different temperatures in an electric furnace and cooled very slowly. The samples of the cobalt oxide obtained at different temperatures were analysed for cobalt by the electrolytic method. The results obtained are given below.

Table I.

Temp.	...	500°	600°	700°	800°	900°
Cobalt (%)	...	76·79	77·55	77·93	78·17	78·47

It appears that cobalt carbonate should be heated up to 900° before a pure sample of cobaltous oxide is formed (% Co in CoO is 78·66).

These samples of oxide, like nickelous oxide, contained some active oxygen which was estimated iodometrically. The amount of active oxygen was found to decrease as the temperature of preparation of the oxide was raised. On applying a correction for this amount of oxygen in the oxide obtained at different temperatures it was found that the oxides obtained at low temperatures did not conform to the theoretical composition.

Like nickelous oxide prepared at low temperature (Prasad and Tendulkar, *loc. cit.*) the samples, obtained at low temperatures, yellow in colour became black when exposed to air. But unlike nickelous oxide, the black colour of the cobalt oxide was not found to disappear when it was treated in an acidified solution of potassium iodide or heated to 500° in vacuum. It is probable that in this case either some different oxide is formed or the attachment of the adsorbed oxygen on the surface of the particles is firm. The low percentage of cobalt obtained in the oxide prepared at low temperatures may thus be mainly due to (*i*) the adsorption of oxygen by the oxide when exposed to air, and (*ii*) the occlusion of gases evolved during the decomposition of the carbonate (*cf.* Richards and Rogers, *J. Amer. Chem. Soc.*, 1893, **15**, 567).

Physical and Chemical Properties of Cobaltous Oxide.

Density.—The oxides prepared at higher temperatures settled in water more quickly than those prepared at lower ones. The experimentally determined densities of the oxides by means of a pyknometer at 28° are given below.

TABLE II.

Temp. (t) ...	500°	600°	700°	800°	900°
$d^{28°}_{4°}$ ...	4·8	5·28	5·6	5·79	6·15

On plotting d against t, it is found that the curve is represented by $d = 0{\cdot}3477\ t^{0{\cdot}4228}$.

Solubility in sulphuric acid.—The solubility of cobaltous oxide was measured in 0·1 *N*-sulphuric acid.

TABLE III.

Temp. ...	500°	600°	700°	800°	900°
CoO dissolved (%) ...	98·35	92·75	83·90	74·65	65·10

It will be seen that the fall in the solubility of the oxide is very rapid as the temperature of preparation is raised from 600° to 900°.

Catalytic decomposition of hydrogen peroxide.—The catalytic effect of cobaltous oxide (*cf.* Nickelous oxide, Prasad and Tendulkar, *loc. cit.*) in the decomposition of hydrogen peroxide was measured in a neutral and an alkaline solution at 30°. The oxide (0·02 g.) was added to 25 c.c. of hydrogen peroxide solution (prepared by tenfold

dilution of Merck's pure 10 volume product) and the rate of decomposition was followed by titrating 2 c.c. of the reaction mixture at definite intervals against $N/100$-$KMnO_4$ solution.

TABLE IV.

Decomposition of H_2O_2 *in a neutral solution*

Time.	H_2O_2 in terms of $N/100$-$KMnO_4$ decomposed by oxide prepared at 500°	600°	700°	800°	900°
10 min.	10·0 c.c.	3·0 c.c.	1·20 c.c.	0·50 c.c.	0·20 c.c.
20	15·5	5·0	2·10	0·70	—
30	19·5	7·0	3·10	0·90	0·60
40	23·0	9·0	4·08	1·15	—
50	—	11·0	4·95	1·60	1·00
60	27·5	13·0	5·90	2·00	—
70	29·0	14·0	7·10	2·60	1·20
80	30·0	15·5	—	—	—
Average value of K (Unimolecular constant)	0·0328	0·0086	0·0035	0·0011	0·00067

TABLE V.

Decomposition of H_2O_2 *in an alkaline solution.*

1·0 C.c. of 0·01N-NaOH added to 25 c.c. of H_2O_2 solution.

Time.	H_2O_2 in terms of $N/100$-$KMnO_4$ decomposed by oxide prepared at 600°	700°	800°	900°
10 min.	7·5 c.c.	3·20 c.c.	2·00 c.c.	1·2 c.c.
20	10·5	4·50	2·50	—
30	13·0	5·35	—	1·8
40	15·5	6·40	3·60	—
50	18·0	7·30	—	2·3
60	20·0	8 30	4·40	—
70	21·5	9·45	—	2·7
80	23·5	—	—	—

The unimolecular constant K was not found to be constant in this case. On plotting x against t the curve is represented by $x = at^{\beta}$ in which the value of β is nearly constant in all the four reactions and the value of a is different for different reactions.

Electrical resistance.—The electrical resistance was measured by Ryschkewitsch's method (*Z. Elektrochem.*, 1926, **32**, 588) and the specific resistance S was calculated in the manner described by Prasad and Tendulkar (*loc. cit.*).

TABLE VI.

t	...	500°	600°	700°	800°	900°
S	...	3170	5200	7300	9250	9880

It will be seen from the foregoing that the physical and chemical properties of the cobalt oxide change immensely when the temperature of preparation of the oxide is changed. The density and the electrical resistance of the oxide increase and the solubility in sulphuric acid and the catalytic decomposition of hydrogen peroxide decrease as the temperature of preparation of the oxide is raised. This increase or decrease is by no means proportional to the change in temperature; only the electrical resistance increases linearly with temperature but this linear relationship no longer holds as the temperature is raised from 800°—900°.

The action of solid substances in a heterogeneous reaction depends upon the size of the particles of the substance. In the present case, although very great care was not taken to use particles of exactly the same size in each experiment, yet the results show a remarkable change in the action of the oxide as the temperature of preparation is altered.

The various causes which are responsible for inducing the inactivity in the oxides as the temperature of the preparation is raised have been discussed by Prasad and Tendulkar (*loc. cit*). Attempts are now being made in this laboratory to account for this induced inactivity.

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Received January 25, 1934.

Complex Compounds of Iridium. Part III. Compounds with Ammonia and Ethylamine.

By Prafulla Chandra Rây and Nadiabehari Adhikari.

By the action of pyridine on $IrCl_3\cdot 3Et_2S$ (*cis*) two compounds $IrCl_3\cdot 2Et_2S\cdot Py$ and $IrCl_3\cdot Et_2S\cdot 2Py$ have been obtained; the remaining diethyl sulphide molecule could not be replaced by pyridine even when the reactants were heated in a sealed tube for 10 hours at 140°-50° (*J. Indian Chem. Soc.*, 1933, **10**, 276). Prolonged heating even at much higher temperature (180°) did not yield better results. The substitution of ethylamine, however, in place of pyridine gives rise to three compounds, *viz.*, (I) ($IrCl_3\cdot 3EtNH_2$), (II) ($IrCl_2\cdot 4EtNH_2$)Cl and (III) ($IrCl\cdot 5EtNH_2$)Cl_2, none of which contains diethyl suphide although this reaction has been carried out at 130°-135° for 3 hours only. If $IrCl_3\cdot 3Et_2S$ in benzene be refluxed with alcoholic ethylamine for 30 hours, a very minute quantity of a greenish yellow substance (m.p. 310° decomp.) soluble in water, is obtained and the rest becomes tarry. When ammonia is passed in the benzene or acetone solution no replacement of the sulphide molecule takes place but at 54° on prolonged action, a minute quantity of a substance, insoluble in benzene, unlike the parent body but containing nitrogen, is obtained. In a sealed tube at 140°-145°, two compounds (IV) ($IrCl_3\cdot Et_2S.2NH_3$) and (V) ($IrCl\cdot 5NH_3$)Cl_2 have been isolated. Palmaer, (*Z. anorg. Chem.*, 1895, **10**, 320; 1897, **13**, 211) obtained compound (V) from iridium trichloride hydrate and ammonia with much difficulty as it is not so easy to have the pure compound free from traces of amonium chloride which invariably forms a part in Palmaer's method. At a still higher temperature, the yield of the compound (V) increases with the corresponding decrease of (IV) and a mixture is obtained which is soluble in cold water and contains iridium and chlorine almost in the invariable ratio of 1 : 3 and nitrogen. In both the cases there remains light yellow filtrate forming a glass like mass in vacuum, very hygroscopic

and containing sulphur and nitrogen. The complete or partial replacement of diethyl sulphide by ethylamine, ammonia, and pyridine, therefore, appears to depend more upon the strength of the bases concerned than on the temperature of the reaction.

The compounds (I—III) are stable, Werner complexes, (II) and (III) giving precipitates with an aqueous silver nitrate. The molecular conductivity of (III) at infinite dilution is 226 which is slightly lower than that of a ternary electrolyte. This may be due to a decreased mobility of the radicle ($IrCl\cdot 5Et\ NH_2$).

The compounds (IV) and (V) are less stable than the others in aqueous solution, both of them give precipitates with aqueous silver nitrate although all the chlorine atoms are supposed to be within the co-ordination group in (IV), *e.g.*

$$\left[\begin{array}{c} Et_2S \diagdown \quad \diagup Cl \\ NH_3 - Ir - Cl \\ Et_2S \diagup \quad \diagdown Cl \end{array}\right]$$

Its solution in water is not acidic, which precludes the possibility of the replacement of chlorine atoms by OH groups and consequent formation of HCl. The only possibility, therefore, is the formation of an aqueo compound which is very common in the ammino compounds of iridium. Moreover, the molecular conductivity of (V) indicates that all the three chlorine atoms ionise in solution to produce ($Ir\cdot 5NH_3,\ H_2O$) Cl_3 (*cf.* Lamb and Fairhall, *J. Amer. Chem. Soc.*, 1923, **45**, 378).

Like most of the iridium ammines compounds (II) and (III), when treated with freshly prepared moist silver oxide, yield strongly basic solutions of light yellow colour. These compounds are strongly alkaline to litmus, liberate ammonia from ammonium salts when gently heated, and absorb carbon dioxide when exposed to the atmosphere; but on standing over silver oxide for 20 hours slowly they turn blue. On acidification of this blue solution, a dark blue precipitate, which may be iridium oxide or hydroxide, is obtained. Iridium chloropentammine chloride yields a stronger and more stable base (Dixon, *J. Chem. Soc.*, 1934, 34). The compound (IV) too, on similar treatment yields a strong base and it is more stable than those derived from compounds (II) and (III) as it does not decompose on standing. It partially precipitates silver hydroxide from aqueous silver nitrate and liberates ammonia from ammonium chloride when gently warmed.

The isolation of different salts of these bases will form the subject of our next communication.

\ ERIMENTAL.

Preparation of $IrCl_3 \cdot 3EtNH_2$, $IrCl_3 \cdot 4EtNH_2$ *and* $IrCl_3 \cdot 5EtNH_2$.—$IrCl_3 \cdot 3Et_2S$(2·8 g.) and ethylamine (5 c.c. of 50% alcoholic solution) were heated in a sealed tube for 8 hours at 140°-145°. The whole mass solidified on cooling and to this alcohol was added (A). The insoluble solid was separated, and was then extracted thrice with boiling water, first time the extraction being continued for 8 hours and 1 hour each for the successive ones. The insoluble substance was then washed with alcohol and ether, m.p. 220° (decomp.), light yellow substance. (Found: N, 9·61; Cl,24·44; Ir, 44·17. $IrCl_3 \cdot 3C_2H_5NH_2$ requires N, 9·66; Cl, 24·4; Ir, 44·3 per cent). The aqueous solution was evaporated to dryness on a water-bath and was thrice recrystallised from hot water. It is sparingly soluble in cold water but readily so when warm, light yellow cubical plates, m.p. 281°-82° (decomp.). (Found: N, 11·56; Cl,21·86; Ir, 40·06. $IrCl_3 \cdot 4C_2H_5NH_2$ requires N, 11·66; Cl,22·1; Ir, 40·22 per cent). To the alcoholic mother liquor (A) ether was added with the separation of an oily substance. This oily substance was dissolved in acetone when a white substance was left behind. This substance was crystallised from water. It gradually decomposes without definite melting point when heated. The acetone solution on spontaneous evaporation yielded the same substance when it was left for 7 days but an oily substance still remained uncrytallised. It is soluble in cold water and when crystallised, it is of very light yellow colour. (Found: N, 12·85; Cl, 20·14; Ir, 36·87. $IrCl_3 \cdot 5C_2H_5NH_2$ requires N, 13·2; Cl,20·35; Ir, 36·76 per cent).

The molar coductivity of $IrCl_3 \cdot 5Et\,NH_2$ at different concentrations in water at 29°,

Molar conc. ...	0·001719	0·0008595	0·0004298
Molar conductivity ...	210·4	216·9	226·6

Preparation of $IrCl_3 \cdot Et_2S \cdot 2NH_3$ *and* $IrCl_3 \cdot 5NH_3$.—$IrCl_3 \cdot 3Et_2S$ (2·5 g.) and liquor ammonia (18 c.c. Merck) in a sealed tube were heated for 6 hours at 135°-145°. When cold a white crystalline substance separated out and a yellow solution with a layer of

diethyl sulphide floating over it was obtained. The sulphide was extracted with ether; the main solution when concentrated over sulphuric acid yielded a light yellow crystalline substance. It is very soluble in water and does not melt when heated but gradually decomposes. It was crystallised twice from a mixture of acetone and water. It precipitates silver chloride from silver nitrate solution. (Found: N, 6·58 ; Cl, 25·0 ; S, 7·64 ; Ir, 45·6. $IrCl_3 \cdot Et_2S \cdot 2NH_3$ requires N, 6·6; Cl, 25·1; S, 7·56; Ir 45·67 per cent). The filtrate from the above could not be crystallised. It is hygroscopic and contains NH_3 and Cl.

The insoluble white substance referred to above was thrice crystallised from boiling water. (Found: N, 18·4; Cl, 27·75; Ir, 50·0. $IrCl_3 \cdot 5NH_3$ requires N, 18·2; Cl, 27·69; Ir, 50·18 per cent.).

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Azotriphenylmethane and Azopyronine Dyes.

(*Ortho* Series).

By Rajendra Nath Sen and Sachindra Nath Roy.

The attempted coupling of *m*-hydroxybenzaldehyde and diazotised aniline has hitherto been unsuccessful, nitrogen being evolved during the process of coupling and no colouring matter being produced (*Ber.*, 1901, **34**, 2094). The evolution of nitrogen, however, can be minimised by cooling the diazotised aniline and *m*-hydroxybenzaldehyde solutions to $-6°$ to $-8°$ and by using sodium carbonate in place of caustic soda, sodium acetate being also added with advantage. With this modification about 10-12% of the theoretical yield of benzene-azo-*m*-hydroxybenzaldehyde has been obtained.

The evolution of nitrogen also takes place with increased vigour during the coupling of diazotised naphthylamines, toluidines, benzidine, etc., with *m*-hydroxybenzaldehyde. It is, however, very interesting to note that when a negative group such as NO_2, Br, SO_3H or COOH group is present in the diazotised amines, the coupling with an alkaline solution of *m*-hydroxybenzaldehyde takes place smoothly with no evolution of nitrogen. Incidentally it may also be pointed out that diazotised amines do not react with *m*-aminobenzaldehyde in acid or alcoholic solutions, the presence of a negative group in the amine seems to have no effect on the coupling in this case.

Regarding the properties of the various *o*-azoaldehydes it has been observed that the presence of a negative group makes the azoaldehyde much more soluble in alkali than the azoaldehyde itself, while in organic solvents the solubility decreases.

The alkaline solution of the nitroazoaldehydes are intense red and possibly a change in the constitution takes place in solution (*cf.* Grandmougin and Guisan, *Rev. Gen. Mat. Col.*, 1908, **12**, 129).

$$NO_2\cdot C_6H_4\cdot N:N\cdot C_6H_3\left\langle\begin{matrix}CHO\\ OH\end{matrix}\right. \xrightarrow{NaOH}$$

$$\left.\begin{matrix}O\\ NaO\end{matrix}\right\rangle N=C_6H_4=N-N=C_6H_3\left\langle\begin{matrix}CHO\\ O\end{matrix}\right.$$

The nitroazoaldehydes also give deep shades on silk and wool unlike the azoaldehydes themselves or their bromo, sulphonic acid or carboxylic acid derivatives which dye silk and wool only in light yellow to brown shades.

These *o*-azoaldehydes have afforded an opportunity of studying the azotriphenylmethane and azopyronine dyes containing azo and the triphenylcarbinol chromophores in *ortho*-positions to each other and also of comparing the effect of the two chromophores in the *ortho*-positions with their effect when occurring in the *para*-positions (Green and Sen, *J. Chem. Soc.*, 1912, **101**, 1113; Sen and Sett, *J. Amer. Chem. Soc.*, 1924, **46**, 111; Dutt, *J. Chem. Soc.*, 1926, **129**, 1171) and in the *meta* positions (Sen and Ghosh, *J. Indian Chem. Soc.*, 1928, **5**, 487; Dutt, *loc. cit.*).

The *o*-azoaldehydes, used in the preparation of the required azotriphenylmethane and azopyronine dyes, have been obtained by coupling *m*-hydroxybenzaldehyde with diazotised (*a*) aniline (*b*) naphthylamine, (*c*) *p*-toluidine and (*d, e, f*) three *o*-, *m*-, and *p*-nitroanilines. These *o*-azoaldehydes (*a, b, c, d, e, f*) have yielded (A) azotriphenylmethane dyes by their condensation with (*i*) dimethylaniline and (*ii*) *o*-cresotinic acid; and (B) azopyronine dyes by their condensation with (*i*) resorcin and (*ii*) pyrogallol. (The condensation with diethyl-*m*-aminophenol was made only with benzene-azo-*m*-hydroxybenzaldehyde.

From a study of the various azotriphenylcarbinol and azopyronine dyes prepared, it has been observed that the introduction of an azo group in the *ortho*-position to the central carbon atom in triphenylcarbinol or pyronine dye, is generally attended with an increase in the depth of colour, much less than in the case of *para*-compounds and almost similar to that of *meta*-compounds.

The influence of nitro groups on the triphenylcarbinol or pyronine dyes is not so marked, though there is a slight alteration in the shade. Thus in the case of *o*-cresotinic acid condensation products, the presence of a nitro group tends to intensify the shade produced by the carbinol on silk or wool while in case of resorcinol and pyrogallol condensation products the presence of nitro group seems to produce a lighter shade on silk.

A great difference between the azotriphenylmethane dyes of the *para* and *ortho* series is that the yellow shade on wool produced by the *leuco* *o*-cresotinic acid compound of the *para* series changes from yellow through maroon to dark-green and black by after-chroming

and the carbinols are remarkably polygenetic (Green and Sen, *loc. cit.*), but the yellow shade produced by the corresponding *leuco* compound in *ortho* series changed only to dirty brown on similar treatment and the carbinols are only feebly polygenetic; and in these respects they are more akin to the corresponding compounds of the *meta* series (Sen and Ghosh, *loc. cit.*).

The condensation product of benzene-azo-*m*-hydroxybenzaldehyde and diethyl-*m*-aminophenol produces a deep pink shade on silk and wool unlike the corresponding compound of the *meta* series, which dyes silk and wool violet (Sen and Ghosh, *loc. cit.*).

Experimental.

Benzene-azo-m-*hydroxybenzaldehyde* (*a*).—A solution of diazotised aniline (10 g.) was slowly added to an alkaline solution (containing Na_2CO_3 together with a little NaOH) of *m*-hydroxybenzaldehyde (13 g.) both cooled to $-5°$ to $-8°$ and the solution well stirred. The solution frothed and swelled up. The precipitated colouring matter was filtered, washed and dried. It was purified from tarry impurities by dissolving in warm glacial acetic acid and reprecipitating by dilution with water. It is obtained as a light brown powder from dilute alcohol and produces light brown shade on wool and silk. It is soluble in alcohol, benzene, chloroform, acetic acid, ether; m.p. 127°, yield 10-12%. (Found: N, 11·72. $C_{13}H_{10}O_2N_2$ requires N, 12·38 per cent).

The *semicarbazone* is yellow in colour, m.p. 250°. (Found: N, 25·37. $C_{14}H_{13}O_2N_5$ requires N, 24·73 per cent).

Naphthalene-1-*azo*-m-*hydroxybenzaldehyde* (*b*).—A solution of diazotised α-naphthylamine (10 g.) was slowly added to an alkaline solution (Na_2CO_3) of *m*-hydroxybenzaldehyde (8·5 g.) both cooled below -5°. The precipitated azo compound was filtered, washed and dried. It was then dissolved in glacial acetic acid and reprecipitated with acidulated water. It was collected, washed and dried and obtained as a chocolate powder from dilute alcohol. It is soluble in benzene, alcohol, chloroform and glacial acetic acid and produces light pink shade on wool and silk, m.p. 167-68°, yield 12-15%. (Found: N, 9·92. $C_{17}H_{12}O_2N_2$ requires N, 10·14 per cent).

The *semicarbazone* is brown, m.p. 251°. (Found: N, 21·86. $C_{18}H_{15}O_2N_5$ requires N, 21·02 per cent).

p-*Toluene-azo*-m-*hydroxybenzaldehyde* (*c*), was prepared by coupling diazotised *p*-toluidine with *m*-hydroxybenzaldehyde. It is

obtained from dilute alcohol as a brown powder, m.p. 180°. It is soluble in alcohol, chloroform, glacial acetic acid and produces yellow shade on silk and wool, yield 15%. (Found: N, 11·09. $C_{14}H_{12}O_2N_2$ requires N, 11·67 per cent).

The *semicarbazone* is brownish yellow, m.p. 251°. (Found: N, 23·04. $C_{15}H_{15}O_2N_5$ requires N, 23·57 per cent).

The preparations of the three compounds, o-*Nitrobenzene-azo*-m-*hydroxybenzaldehyde* (*d*), m-*Nitrobenzene-azo*-m-*hydroxybenzaldehyde* (*e*) and p-*Nitrobenzene-azo*-m-*hydroxybenzaldehyde* (*f*) are exactly similar.

A diazotised solution of *p*-nitroaniline (10 g.) was poured into an alkaline (NaOH) solution of *m*-hydroxybenzaldehyde (9 g.) cooled to 0°. A deep red solution was obtained and *no frothing took place.* The azo compound remained in solution as the Na-salt which was obtained on evaporating a portion on a water-bath. The free azo-compound was precipitated on acidifying the solution with dilute acetic acid. It was filtered, washed and dried and finally purified from dilute alcohol. It is soluble in benzene, alcohol, glacial acetic acid and chloroform. The p-*nitro compound* crystallises in bright yellow needles, m.p. 175°. It produces golden yellow shade on silk and wool. (Found: N, 15·95. $C_{13}H_9O_4N_3$ requires N, 15·52 per cent). The *semicarbazone* is a yellow solid and crystallises in needles, m.p. 246°. (Found: N, 26·49. $C_{14}H_{12}O_4N_6$ requires N, 25·61 per cent).

The o-*nitro compound* crystallises in orange needles, m.p. 150-51°. It produces orange shade on silk and wool. (Found: N, 15·55. $C_{13}H_9O_4N_3$ requires N, 15·52 per cent). The *semicarbazone* is a yellowish orange solid and crystallises in needles, m.p. 260°. (Found: N, 25·53. $C_{14}H_{12}O_4N_6$ requires N, 25·61 per cent).

The m-*nitro compound* crystallises in brownish red needles, m.p. 180°. It produces yellowish orange shade on silk and wool. (Found: N, 15·19. $C_{13}H_9O_4N_3$ requires N, 15·52 per cent). The *semicarbazone* is obtained as light yellow needles, m.p. 243°. (Found: N, 26·07. $C_{14}H_{12}O_4N_6$ requires N, 25·61 per cent).

p-*Bromobenzene-azo*-m-*hydroxybenzaldehyde* (*g*), o-*Carboxybenzene-azo*-m-*hydroxybenzaldehyde* (*h*) and p-*Sulphonic acid benzene-azo*-m-*hydroxybenzaldehyde* (*i*).—A diazotised solution of *p*-bromoaniline (6 g.) or anthranilic acid (4·5 g.) or sulphanilic acid (5·5 g.) was slowly added to an alkaline (NaOH) solution of *m*-hydroxybenzaldehyde (4·2 g.) to prepare the compounds (*g*), (*h*) and (*i*) respectively. The

azo compounds which remained in solution were precipitated by acidifying the solution with dilute acetic acid in cases of (*g*) and (*h*). The compounds were purified in the same way as *p*-nitrobenzene-azo-*m*-hydroxybenzaldehyde (*f*) and purified from dilute alcohol. In case of (*i*) the compound separated on exactly neutralising the alkaline solution with dilute hydrochloric acid and concentrating on a water-bath. The compound (*g*) is a yellowish brown powder, m. p. 130°, producing yellow shade on silk and wool. The compound (*h*) is a reddish brown powder, m. p. 162°, producing yellow shade on silk and wool. As these three compounds were difficult to purify they could not be analysed.

Triphenylmethane Dyes.

Condensation of the azoaldehydes (a—f) with dimethylaniline (1—6).—The aldehyde (1 mol.) was mixed with dimethylaniline (2 mol.) and a small quantity of concentrated HCl, just insufficient to neutralise the dimethylaniline and the solution was heated for 12 to 18 hours at 100-115°. The solution was then made strongly alkaline with caustic soda and was distilled in steam to remove any excess of dimethylaniline. The precipitated *leuco* compound was then washed by decantation, dried and purified from a mixture of chloroform and petroleum ether (1:1). It is sparingly soluble in ether and benzene but highly soluble in chloroform.

The *leuco* compound is oxidised to the carbinol stage by adding calculated amount of lead peroxide to a solution of the former in a mixture of hydrochloric and acetic acid in the cold.

Condensation of the azoaldehydes (a—f) with o-*cresotinic acid* (7—12).—The azoaldehyde (1 mol.) was intimately mixed with *o*-cresotinic acid (2 mol.) and the mixture was made pasty with concentrated sulphuric acid (*d* 1·84), kept for 24 hours and then treated with ice-cold water. The product was dissolved in caustic soda solution, filtered, reprecipitated with dilute hydrochloric acid and filtered again. The finely powdered dry product was purified by repeated washing with hot benzene. It is obtained as a yellowish brown powder from dilute alcohol.

The carbinol compound was obtained by condensing the aldehyde with *o*-cresotinic acid in the cold in presence of concentrated sulphuric acid as above and then adding requisite amount of nitrosyl sulphate

to the mixture and then heating to 70-80° till the oxidation was complete. It was then isolated and purified exactly in the same way as in the case of the *leuco* compound and was finally washed with hot alcohol in which it is but sparingly soluble. The compounds are described in the Table I.

Pyronine Dyes.

Condensation of the azoaldehydes (a—f) with resorcinol (13—18).—The *o*-azoaldehyde(1 mol.) was intimately mixed with resorcinol (2 mol.) and a paste was made with sulphuric acid (*d* 1·84) and was heated at 120-130° for 8 to 10 hours, sulphuric acid acting as the condensing as well as the oxidising agent (Sen and Sinha, *J. Amer. Chem. Soc.*, 1923, 43, 2984). The mixture was cooled and treated with cold water. The product was dissolved in caustic soda, filtered, reprecipitated with hydrochloric acid and again filtered and dried. It was then powdered and washed repeatedly with hot benzene and chloroform in which it is insoluble.

Condensation of the azoaldehydes (a—f) with pyrogallol (19—24).—The method of preparation is similar to that followed in the case of condensation with resorcinol. The condensed products are in all cases insoluble in ordinary solvents. None melts below 300°. The compounds are described in the Table I.

Names of compounds.	M. p. (decomp.).	Analysis. Found.	Analysis. Calc.	Shade on wool and silk.	Remarks.
Cond. products (*leuco*) of dimethylaniline with azoaldehydes.					
1. 1-Benzene-azo-4-hydroxy-8:13-tetramethyldiaminotriphenylmethane (*a*)	95-100	N, 11·70	12·45	Green	Shades produced by carbinols. These also dye tannined cotton.
2. 1-Naphthaleneazo-4-hydroxy-8 :13-tetramethyldiaminotriphenylmethane (*b*)	,,	10·4	11·2	Bluish green	
3. 1-*p*-Toluene-azo-4-hydroxy-8 :13-tetramethyldiaminotriphenylmethane (*c*)	120-25	11·42	12 07	Green	
4. 1-*o*-Nitrobenzene-azo-4-hydroxy-8:13-tetramethyldiaminotriphenylmethane (*d*)	100-10	14·98	14·14	Green	
5. 1-*m*-Nitrobenzene-azo-4-hydroxy-8 :13-tetramethyldiaminotriphenylmethane (*e*)	100-10	14·70	14·14	Green	
6. 1-*p*-Nitrobenzene-azo-4-hydroxy-8:13-tetramethyldiaminotriphenylmethane (*f*)	100-10	14·17	14·14	Green	
Cond. products (leuco) of *o*-cresotinic acid with the azoaldehydes.					
7. 1-Benzene-azo-4 :8 :13-trihydroxy-9 :12-dimethyl-7 :14-dicarboxytriphenylmethane (*a*)	208	5·82	5·47	Deep orange	Shades produced by carbinols. The corresponding carbinols of 7 & 8 in the *p*-series produce red shade (Green and Sen, *loc. cit.*) and in the *m*-series reddish orange shade. All the carbinols are weakly polygenetic.
8. 1-Naphthalene-azo-4 :8:13-trihydroxy-9:12-dimethyl-7 :14-dicarboxytriphenylmethane (*b*)	200	5·00	4·98	Brownish orange	
9. 1-*p*-Toluene-azo-4 :8:13-trihydoxy-9 :12-dimethyl-7 :14-dicarboxytriphenylmethane (*c*)	210	5·50	5·32	Reddish brown	
10. 1-*o*-Nitrobenzene-azo 4 :8 :13-trihydroxy-9 :12-dimethyl- :14-dicarboxytriphenylmethane (*d*)	213	7·50	7·54	,,	
11. 1-*m*-Nitrobenzene-azo-4:8:13-trihydroxy-9 :12-dimethyl-7 :14-dicarboxytriphenylmethane (*e*)	212	6·94	7·54	,,	
12. 1-*p*-Nitro-benzene-azo-4 :8 :13-trihydroxy-9 :12-dimethyl-7:14-dicarboxytriphenylmethane (*f*)	212	7·56	7·54	,,	

Names of compounds.	M. p.	Analysis. Found.	Analysis. Calc.	Shades on wool and silk.	Remarks.
Cond. products of resorcinol with the azoaldehydes.					
13. (a)	Does not melt below 300°.	N, 5·97	6·86	Brownish red	Alkaline solutions of 13, 14 & 15 are fairly fluorescent but those of 16, 17 & 18 are only very feebly fluorescent, possibly due to the presence of NO_2 groups. Azo groups in the *o*-position increase the depth of colour but diminish fluorescence.
14. (b)		5·25	6·11	Reddish orange	
15. (c)		6·31	6·61	Brownish red.	
16. (d)		9·25	9·27	Reddish yellow	
17. (e)		8·88	9·27	,,	
18. (f)		9·08	9·27	,,	
Cond. products of pyrogallol with the azoaldehydes.					
24. (a)	Does not melt below 300°.	5·58	6·86	Greyish black	Shades on iron-mordanted wool feebly polygenetic.
23. (b)		5·57	5·71	,,	
22. (c)		5·45	6·17	,,	
21. (d)		8·78	8·66	,,	
20. (e)		8·65	8·66	,,	
19.		9·07	8·66	,,	

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Condensation of Chloral and Bromal Hydrates with Amides.

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In extension of a study of the condensation of chloral with amides by Meldrum and Bhojraj (*Proc. Indian Science Congress*, 1926, p. 146) the authors have prepared a number of chloral and bromalamides and have examined their chemical properties.

Chloralacetamide was prepared by Pinner (*Ber.*, 1877, **10**, 1968) by the action of ammonia on chloralacetyl chloride and by Schiff and Tassinari (*ibid.*, p. 168) from chloralammonia and acetyl chloride. Jacobson (*Annalen*, 1871, **157**, 245) prepared chloralacetamide and chloralbenzamide from chloral and respective amides. The authors have prepared chloralamides and bromalamides by heating an equimolecular mixture of chloral or bromal hydrate and amides till a solid was obtained. Dichloralmalonamide and dichloralsuccinamide were obtained by heating under reflux a mixture of the finely powdered amide with chloral. Dichloralmalonamide formed a paste which set to a glassy mass which on keeping in water for several days gave a solid. Bromalsalicylamide and bromal-*o*-methoxybenzamide also formed pastes solidifying on treatment with water.

The anhydro derivatives of chloralamides were first obtained by Moscheles (*Ber.*, 1891, **24**, 1803) by the action of acetic anhydride in cold sodium hydroxide solution. Moscheles (*loc. cit.*), Hantzsch (*Ber.*, 1894, **27**, 1248), Diels and Seib (*Ber.*, 1909, **42**, 4062) and Diels and Gukassianz (*Ber.*, 1910, **43**, 3314) gave the anhydro derivatives the constitution $R\cdot CO\cdot N:CH\cdot CCl_3$. Feist (*Ber.*, 1912, **45**, 945) showed that the products have the constitution $(R\cdot CO\cdot NH\ CH\cdot CCl_3)_2O$. It has been found by the authors that one molecule of chloralsalicylamide loses one molecule of water to form an anhydro derivative while other chloralamides and bromalamides lose water in the way that Feist observed, two molecules lose one molecule of water and form an anhydro derivative.

Previous workers using acetyl chloride in presence of sodium hydroxide solution obtained the anhydro derivatives while the acetyl derivatives were obtained, if at all, as a by-product. The authors prepared

the acetyl derivatives (*i*) by dissolving the chloral or bromalamides in pyridine and adding acetyl chloride, (*ii*) by the action of acetic anhydride containing sulphuric acid. Chloralsalicylamide gave by both the methods the anhydro compound which absorbed bromine. It gave the acetyl derivative by keeping it with acetic anhydride and sulphuric acid for a few days. Diacetylchloralsalicylamide was obtained by heating chloralsalicylamide with acetic anhydride in presence of sulphuric acid. Bromal-*o*-methoxybenzamide gave with acetic anhydride in sodium hydroxide solution a mixture of the acetyl and the anhydro derivatives from which the components were separated by fractional crystallisation from ethyl acetate.

The methyl ethers were obtained from the chloral or bromalamides with dimethyl sulphate in presence of dilute sodium hydroxide solution (*cf*. Feist, *loc. cit.*).

The reduction products were obtained by stirring the chloral and bromalamides with acetic acid and zinc dust. In the case of chloral-*p*-toluamide the reduction mixture was kept in hot water while in the case of bromalsalicylamide and bromal-*o*-methoxybenzamide the temperature was not allowed to rise above 87°. In the case of other bromalamides the reduction mixture was kept at 15°. The group $CH(OH)\cdot CCl_3$ is changed on reduction to $CH:CCl_2$ and the group $CH(OH)\cdot CBr_3$ to $CH:CBr_2$ or $CH:CHBr$ as shown by Yelburgi and Wheeler (*J. Indian Chem. Soc.*, 1934, 11, 217). The compounds prepared are summarised in the following Tables.

TABLE I.

Name.	Formula.	Appearance.	M. p.	Analysis. Found.	Analysis. Calc.
Dichloralmalonamide	$C_7H_8O_4N_2Cl_6$	Plates	171	Cl 53·6 %	53·6 %
Dichloralsuccinamide	$C_8H_{10}O_4N_2Cl_6$	Plates	172	51·7	51·8
Benzoylchloralacetamide	$C_{11}H_{10}O_3NCl_3$	Long plates	101-02	34·1	34·3
Acetylchloral-*n*-butyramide	$C_8H_{12}O_3NCl_3$	Needles	84-86	38·6	38·5
Benzoylchloral-*n*-butyramide	$C_{13}H_{14}O_3NCl_3$	Needles	126-27	31·2	31·5
Methylchloral-*n*-butyramide	$C_7H_{12}O_2NCl_3$	Needles	94-95	42·9	42·8
Anhydrochloral-*n*-butyramide	$C_{12}H_{18}O_3N_2Cl_6$	Needles	173-74	47·1	47·2
Acetylchloralbenzamide	$C_{11}H_{10}O_3NCl_3$	Needles	153-54	34·3	34·3
Chloral-*p*-toluamide	$C_{10}H_{10}O_2NCl_3$	Hexagonal plates	152	37·5	37·7
β-Dichloroethylene-*p*-toluamide	$C_{10}H_9ONCl_2$	Long plates	101	30·5	30·8
Acetylchloralphenylacetamide	$C_{12}H_{12}O_3NCl_3$	Needles	152	32·9	32·8
Benzoylchloralphenylacetamide	$C_{17}H_{14}O_3NCl_3$	Needles	164	27·6	27·5
Diacetylchloralsalicylamide	$C_{13}H_{13}O_5NCl_3$	Needles	134	28·8	28·9
Andhydrochloralsalicylamide	$C_9H_6O_2NCl_3$	Long plates	174-75	39·9	39 9
Acetylanhydrochloralsalicylamide	$C_{11}H_8O_3NCl_3$	Plates	53-55	34·3	34·5

TABLE II.

Name.	Formula.	Appearance.	M. p.	Analysis. Found.	Analysis. Calc.
Acetylbromalacetamide	$C_6H_8O_3NBr_3$	Square plates	120	Br, 62·3 %	62·5 %
Bromal-*n*-butyramide	$C_6H_{10}O_2NBr_3$	Rhombic plates	145	57·7	57·8
Bromalbenzamide	$C_9H_8O_2NBr_3$	Rhombic plates	148	59·6	59·7
Acetylbromalbenzamide	$C_{11}H_{10}O_3NBr_3$	Needles	142	54·1	54·0
Benzoylbromalbenzamide	$C_{16}H_{12}O_3NBr_3$	Needles	164-65	47·3	47·4
Methylbromalbenzamide	$C_{10}H_{10}O_2NBr_3$	Needles	140-41	57·7	57·8
Anhydrobromalbenzamide	$C_{18}H_{14}O_3N_2Br_3$	Plates	199 (decomp.)	61·0	60·9
β-Bromoethylenebenzamide	C_9H_8ONBr	Needles	122-23	35·2	35·4
Bromal-*p*-toluamide	$C_{10}H_{10}O_2NBr_3$	Hexagonal plates	151	57·4	57·7
β-Bromoethylene-*p*-toluamide	$C_{10}H_{10}ONBr$	Long plates	128-29	33·2	33·3
Bromalphenylacetamide	$C_{10}H_{10}O_2NBr_3$	Rhombic plates	146	57·7	57·8
Acetylbromalphenylacetamide	$C_{12}H_{12}O_3NBr_3$	Tiny needles	151	52·2	52·4
Benzoylbromalphenylacetamide	$C_{17}H_{14}O_3NBr_3$	Needles	143	46·3	46·1
Methylbromalphenylacetamide	$C_{11}H_{12}O_2NBr_3$	Long plates	127-28	55·8	55·8
Anhydrobromalphenylacetamide	$C_{20}H_{18}O_3N_2Br_6$	Long plates	150	58·9	58·9
β-Bromoethylenephenylacetamide	$C_{10}H_{10}ONBr$	Needles	115-16	33·3	33·3
Bromalsalicylamide	$C_9H_8O_3NBr_3$	Cubes	161	57·3	57·4
β-Dibromoethylenesalicylamide	$C_9H_7O_2NBr_2$	Feathery plates	177	49·3	49·8

TABLE II. (*contd.*)

Formula.	Appearance.	M. p.	Analysis. Found.	Analysis. Calc.
$C_{10}H_{10}O_3NBr_3$	Cubes or plates	141-42	Br, 55·5 %	55·6 %
$C_{12}H_{12}O_4NBr_3$	Square plates	115-17	50·6	50·6
$C_{11}H_{12}O_3NBr_3$	Long plates	103-04	53·7	53·8
$C_{20}H_{18}O_5N_2Br_6$	Needles	185-86	56·8	56·7
$C_{10}H_9O_2NBr_2$	Needles	128	47·3	47·7

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Derivatives of Hydroxybenzoic Acids.

By N. Hurry and (late) A. N. Meldrum.

Chloral has been condensed with certain aromatic acids, *viz.*, *m*-hydroxybenzoic acid and its alkyl derivatives (Fritsch, *Annalen*, 1897, **296**, 344). Subsequently Meldrum and Alimchandani studied condensations with gallic acid (*J. Chem. Soc.*, 1920, **117**, 964) and cresotic acids (*J Indian Chem. Soc.*, 1925, **2**, 9). The condensation products in most of these cases were phthalides.

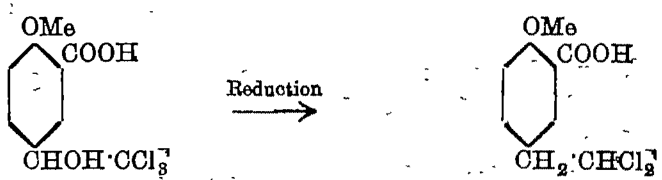
The present work deals with the condensation of chloral with *o*-, *m*-, and *p*- methoxybenzoic acids and *p*-hydroxybenzoic acid. It was undertaken with a view to study the properties of the condensation products and of the $CHOH{\cdot}CCl_3$ group.

One molecule of *o*-methoxybenzoic acid was condensed with one molecule of chloral in presence of sulphuric acid to 2-methoxy-5-$\alpha\alpha\alpha$-trichloro-β-hydroxyethylbenzoic acid (I).

Several unsuccessful attempts were made to oxidise (I) to a ketonic acid by (*i*) Fenton's reagent, (*ii*) dilute and concentrated nitric acid, and (*iii*) alkaline potassium permanganate solution. With the first two reagents the substance was recovered unchanged, but with alkaline permanganate 4-methoxy*iso*phthalic acid (m. p. 265°) was obtained, thus fixing the position of the chloral group.

Attempts were made to hydrolyse the $CHOH{\cdot}CCl_3$ group using various strengths of sodium hydroxide, potassium hydroxide and barium hydroxide solutions, but the yields were poor. The period of heating on a water-bath was varied from 3 hours to 7 days and finally the mixture was heated at 110°, 120°, 130° and 140°; granular crystals were obtained, m. p. 263°, the melting point was lowered by admixture with 4-methoxy*iso*phthalic acid. The equivalent agreed with the formula $OMe{\cdot}C_6H_3{\cdot}COOH{\cdot}CHOH{\cdot}COOH$.

The compound (I) on reduction with zinc and glacial acetic acid (*cf.* Meldrum and Alimchandani, *J. Indian Chem. Soc.*, 1925, **2**, 9) gave 2-methoxy-5-$\alpha\alpha$-dichloroethylbenzoic acid (II).



(I) (II)

On fusion with sodium hydroxide (II) gave 4-methoxy-5-carboxyphenylacetaldehyde, while on oxidation with fuming nitric acid it gave 4-methoxy*iso*phthalic acid.

The condensation products of *m*-hydroxy-and *m*-methoxybenzoic acids and chloral were respectively 5-hydroxy-and 5-methoxytrichloromethylphthalides which were reduced to 3-hydroxy- and 3-methoxy-6-αα-dichloroethylbenzoic acids. The latter was further reduced by sodium amalgam to 3-methoxy-6-ethylbenzoic acid.

The condensation product of *p*-methoxybenzoic acid and chloral was reduced to 3-ααα-trichloro-β-hydroxyethyl-4-methoxybenzoic acid which was reduced to 3-αα-dichloroethyl-4-methoxybenzoic acid.

It is thus evident that an additional carboxyl group can be inserted in a certain aromatic acid by condensing that acid with chloral and then by oxidation. It is also possible to insert a dichloroethyl group by suitable reduction of $CHOH\cdot CCl_3$ group.

EXPERIMENTAL.

The three hydroxybenzoic acids were methylated according to the method of Meldrum and Shah (*J. Chem. Soc.*, 1923, **123**, 1991; Graebe, *Annalen*, 1905, **349**, 249).

o-Methoxybenzoic acid (30 g.), chloral (40 g.) and sulphuric acid (75 c.c.) were mixed and kept for 48 hours. On dilution a resinous product was obtained which when crystallised from glacial acetic acid gave *2-methoxy-5-ααα-trichloro-β-hydroxyethylbenzoic acid* (I). It crystallised in small needles, m. p. 216°, yield 15 g. It is soluble in alcohol, acetone, chloroform and insoluble in ether and benzene. (Found: Cl, 35·5; Equiv., 302·6. $C_{10}H_9O_4Cl_3$ requires Cl, 35·5 per cent. Equiv., 299·5).

The potassium salt was obtained as plates. (Found: K, 12·0. $C_{10}H_8O_4Cl_3K$ requires K, 11·6 per cent).

The barium salt was obtained by adding barium acetate solution to a neutral solution of the ammonium salt as small needles. (Found: Ba, 17·9; H_2O, 7·0. $C_{20}H_{16}O_8Cl_6Ba$, H_2O requires Ba, 17·4; H_2O, 6·8 per cent).

The calcium salt was crystallised from hot water as granules. (Found: Ca, 5·2; H_2O, 14·6. $C_{20}H_{16}O_8Cl_6Ca$, $6H_2O$ requires Ca, 5·4; H_2O, 14·5 per cent).

The acetyl derivative was obtained as granular crystals, m. p. 143°. (Found: Cl, 31·2 per cent. Equiv., 341·4).

The methyl ester was prepared by refluxing the acid (10 g.), methyl alcohol (35 g.) and dry hydrochloric acid gas (3 g.) on a water-bath for 5 hours. It was crystallised from methyl alcohol in plates, m. p. 145°. (Found: Cl, 33·6. $C_{11}H_{11}O_3Cl_3$ requires Cl, 33·9 per cent).

The ethyl ester crystallised from ethyl alcohol in needles, m. p. 157°. (Found: Cl, 32·2. $C_{12}H_{13}O_3Cl_3$ requires Cl, 32·4 per cent).

The amide.—Methyl ester (5 g.) ammonia (*d* 0·88, 120 c.c.) and absolute alcohol (50 c.c.) were shaken for 40 hours when the amide precipitated as a fine powder. It crystallised in tiny needles from alcohol, m. p. 241°. (Found: Cl, 35·3. $C_{10}H_{10}NCl_3$ requires Cl, 35·7 per cent).

2-*Methoxy-5-ααα-trichloro-β-chloroethylbenzoic acid.*—The acid (2 g.) was heated with thionyl chioride (1·5 g.) at 60° for 4 hours and the acid chloride thus obtained was hydrolysed and crystallised in needles from glacial acetic acid, m. p. 132°. (Found: Cl, 44·3; Equiv., 317·9. $C_{10}H_8O_3Cl_4$ requires Cl, 44·6 per cent. Equiv., 317·9).

The anilide was prepared by pouring the acid chloride mixture, obtained above, into aniline. The anilide crystallised in needles from alcohol, m. p. 154°. (Found: Cl, 36·2. $C_{16}H_{13}O_2NCl_4$ requires Cl, 36·1 per cent).

The p-*toluidide*, prepared by adding the acid chloride mixture to *p*-toluidine in pyridine, crystallised in small plates from alcohol, m. p. 184°. (Found: Cl, 34·6. $C_{17}H_{15}O_2NCl_4$ requires Cl, 34·8 per cent).

Oxidation of (I).—The acid (5 g.) was dissolved in potassium hydroxide (4 g. in 50 c.c. water) and potassium permanganate (4 g. in 50 c.c. water) was gradually added. Sulphur dioxide was passed through the solution after 48 hours and the filtrate was concentrated and acidified when 4-methoxy*iso*phthalic acid was obtained, m. p. 265° (Jacobsen, *Ber.*, 1878, **11**, 899 ; Schall, *Ber.*, 1879, **12**, 828). (Found: Eqiv., 98·9. $C_9H_8O_5$ requires Eqiv., 98·0). The calcium salt crystallised in needles from hot water. (Found: Ca, 14·9; H_2O, 13·2. $C_9H_6O_5Ca, 2H_2O$ requires Ca, 14·8; H_2O, 13·3 per cent).

Hydrolysis of (I).—The acid (5 g.) was heated with potassium hydroxide (4 g. in 23 c.c. water) at 100° for 6-8 hours. The filtrate was acidified with dilute hydrochloric acid when *4-methoxy-5-carboxy-phenylglycollic acid* was obtained in poor yield. The product collected

from several experiments was crystallised from glacial acetic acid, m. p 263°. (Found: Equiv., 112·7. $C_{10}H_{10}O_6$ requires Equiv., 113·0).

Reduction of (I): *Formation of 2-methoxy-5-αα-dichloroethylbenzoic acid* (II).—The acid (15 g.) was reduced in glacial acetic acid (80 c.c.) solution using zinc dust (8 g.) and the mixture was stirred for 3 hours. The product obtained on diluting the filtrate crystallised in needles from glacial acetic acid, m. p. 127°, yield 69%. (Found: Cl, 28·8; Equiv., 250. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·5 per cent. Equiv., 249).

The methyl ester crystallised in small needles, m.p. 57°. The above ester was also prepared by reducing the corresponding ester of (I). (Found: Cl, 26·7. $C_{11}H_{12}O_3Cl_2$ requires Cl, 26·9 per cent).

The amide was prepared similarly to the amide of (I). It crystallised in needles from alcohol, m. p. 147°. It was also prepared by reducing the corresponding amide of (I). (Found: Cl, 28·3. $C_{10}H_{10}O_2NCl_2$ requires Cl, 28·6 per cent).

The anilide.—The acid chloride mixture obtained by treating (II) with thionyl chloride was added to aniline. It crystallised in needles from alcohol, m. p. 105°. (Found: Cl, 22·0. $C_{16}H_{15}O_2Cl_2$ requires Cl, 21·9 per cent).

The p-*toluidide* was obtained as small brown plates, m. p. 115°. (Found: Cl, 20·8. $C_{17}H_{17}O_2NCl_2$ requires Cl, 21·0 per cent).

Hydrolysis of the methoxy group of (II).—5 G. of (II) were treated with hydroiodic acid (20 c.c.) at 125° and *2-hydroxy-5-αα-dichloroethylbenzoic acid* crystallised from acetic acid, m. p. 166°. (Found: Cl, 29·9; Equiv., 234·8. $C_9H_8O_3Cl_2$ requires Cl, 30·2 per cent. Equiv., 235·0).

Fusion of (II) *with alkali*: *Isolation of 3-carboxy-4-methoxyphenylacetaldehyde.*—3 G. of (II) were heated at 165° for ½ hour with powdered sodium hydroxide (2 g.) in water (2 c.c.) The filtrate on acidification gave the aldehyde, which was crystallised from acetic acid, m.p. 165°. (Found: Equiv., 210·4. $C_{10}H_{10}O_4$, H_2O requires Equiv., 212·1).

The potassium salt contains one and a half molecule of water. (Found: K, 15·0; H_2O, 10·1. $C_{10}H_9O_4K$, $1\frac{1}{2}H_2O$ requires K, 15·1; H_2O, 10·4 per cent).

Oxidation of (II).—5 G. of (II) were dissolved in fuming nitric acid and kept at 100° for 1 hour. It was cooled and diluted when *5-methoxyisophthalic* acid was obtained, m. p. 265°.

3-*Hydroxy-6-αα-dichloroethylbenzoic acid* was prepared by the reduction of 5 g. of 5 hydroxytrichloromethylphthalide (condensation product of *m*-hydroxybenzoic acid with chloral. Fritsch, *loc. cit.*) with zinc dust (3 g.) and glacial acetic acid (30 c.c.). It crystallised in needles from dilute acetic acid, m. p. 194°. (Found: Cl, 30·2. $C_9H_7O_3Cl_2$ requires Cl, 30·2 per cent).

3-*Methoxy-6-αα-dichloroethylbenzoic acid* (III) was prepared by the reduction of 5-methoxytrichloromethylphthalide (condensation product of *m*-methoxybenzoic acid with chloral, m.p. 135°) with zinc and acetic acid. It crystallised in needles from acetic acid, m. p. 165°, yield 7·4 g. (Found: Cl, 28·6; Equiv., 250. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·5 per cent. Equiv., 249).

The sodium salt was obtained as small needles. (Found : Na, 8·6. $C_{10}H_9O_3Cl_2Na$ requires Na, 8·5 per cent).

The methyl ester was obtained by refluxing (III) (3 g.) in methyl alcohol (25 c.c.) containing dry hydrochloric acid (2 g.) for 5 hours. It crystallised in needles from alcohol, m. p. 88°. (Found: Cl, 26·8. $C_{11}H_{12}O_3Cl_2$ requires Cl, 27·0 per cent).

The ethyl ester crystallised in needles from alcohol, m. p. 64°. (Found: Cl, 25·5. $C_{12}H_{14}O_3Cl_2$ requires Cl, 25·6 per cent).

The anilide.—2G. of (III) and thionyl chloride (1·5 g.) were heated at 60° for 4 hours and the mixture was added to aniline. It crystallised in needles from alcohol, m. p. 118°. (Found: Cl, 21·6. $C_{16}H_{15}O_2NCl_2$ requires Cl, 21·9 per cent).

Further reduction of (III): *Isolation of 3-methoxy-6-ethylbenzoic acid.*—5 G. of (III) were further reduced by sodium amalgam. A current of carbon dioxide was passed into the solution to keep it neutral. The substance obtained on acidifying was crystallised from chloroform to remove a compound containing chlorine, which is present in a small quantity, and it was finally crystallised from alcohol as granules, m. p. 87°. (Found: Equiv., 190·5. $C_{10}H_{12}O_3$ requires Equiv., 190·1).

3-$\bar{\alpha}\bar{\alpha}\bar{\alpha}$-*Trichloro-β-hydroxyethyl-4-methoxybenzoic acid.*—Anisic acid (40 g.) and chloral (55 g.) were kept for 72 hours in presence of sulphuric acid (80 c.c.) The acid obtained on dilution was crystallised thrice from acetone as granules; shrinks at 161° and melts at 275°. (Found: Cl, 35·5; Equiv., 300·6. $C_{10}H_9O_4Cl_3$ requires Cl, 35·5 per cent. Equiv., 299·5),

3-*αα̃-Dichloroethyl-4-methoxybenzoic acid.*—The above acid (10 g.) was reduced by zinc dust (6 g.) and acetic acid (70 c.c.). It separated from glacial acetic acid or 50% alcohol in granules. It is soluble in acetone, shrinks at 210° and melts at 221°. (Found: Cl, 28·3; Equiv., 250·5. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·5 per cent. Equiv., 249).

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Antimony and Mercury Compounds of Quinoline and *iso*Quinoline.

By Rajendra Nath Sen and Gopal Krishna Mukherjee.

The present investigation was undertaken with the object of introducing antimony in quinoline and *iso*quinoline nuclei and by the application of Bart's reaction it has been possible to introduce antimony into 3-, 5-, 6-, 7- and 8- positions of the quinoline nucleus. But as during the course of the investigation Morgan and Cook's paper (*J. Chem. Soc.*, 1930, 737) dealing with quinolyl-5-, 6- and 8- stibinic acids has already appeared only the sodium salts of the corresponding 7-and 5-derivatives are described in this paper.

It has been observed that the position of the amino group in the quinoline nucleus is of very great consequence. Thus 2- and 4-aminoquinolines do not even respond to the diazo reaction (Mills and Watson, *J. Chem. Soc.*, 1910, **97**, 741; Claus and Frobenious *J. pr. Chem.*, 1897, ii, **56**, 191; Wenzel, *Monatsh.*, 1894, **15**, 458), the 6 and 8-aminoquinolines yield only 10 to 15% of the stibinic acids (sodium salt) while 25-30% of the corresponding stibinic acids are obtained from 3-, 5- and 7-aminoquinolines. In the case of *iso*quinoline, however, the yield of the stibinic acid (sodium salt) is comparatively small, being only 5-8% of the theoretical. All the stibinic acids in the free state are more or less amorphous substances though they give sodium salts, which possess well-defined crystalline shape and contain water of crystallisation. It is also interesting to note that the crystalline sodium salts containing water of crystallisation are more or less coloured. The colour of the salts practically disappears on heating due to loss of water of crystallisation but none of them melts or decomposes even at 300°.

It has also been possible to obtain quinoline derivatives with a mercury atom in the nucleus by the action of mercuric acetate on 8-oxyquinoline, the mercury atom entering the quinoline nucleus into the *ortho* or the *para* position to the hydroxyl group, probably in the latter as in the case of α-naphthol which usually gives the *para* compound. Hydroxymercuro-8-oxyquinoline sulphonic and carboxylic acids and a number of allied compounds have also been prepared by Heyden (D. R. P. 289246). Dede and Hessler (*Z. anorg. Chem.*, 1930, **188**, 325) have also described compounds of the type $(C_9H_6ON)HgCl_3$ (C_9H_7ON) prepared from 8-oxyquinoline and mercuric salts.

5-Bromo-8-oxyquinoline and 5:6-dibromo-8-oxyquinoline have been mercurated and it has been found that they also undergo mercuration as easily as 8-oxyquinoline, the mercury atom evidently entering into the *ortho* position to the hydroxyl group. The bromo-oxyquinolines were prepared by brominating 8-oxyquinoline (Claus and Howitz, *J. pr. Chem.*, 1891, *ii*, **44**, 433).

That in these compounds the mercury atom is not attached to the oxygen atom is proved by the stability of these comounds towards caustic alkalis, the *o*-mercury compounds being decomposed in the presence of caustic alkali (*cf.* Neogi and Chatterji, *J. Indian Chem. Soc.*, 1928, **5**, 221). These compounds are soluble in caustic alkalis instead of being decomposed by them.

These acetoxymercuri derivatives are amorphous powder, insoluble in water and in common organic solvents. On heating they decompose with the liberation of mercury.

Experimental.

Sodium quinolyl-7-stibinate.—7-Aminoquinoline (5 g.) was dissolved in 100 c. c. of dilute hydrochloric acid (1:1) and diazotised. Antimony trichloride solution prepared by dissolving antimony trioxide (5 g.) in concentrated hydrochloric acid (19 c. c.) was added slowly with stirring to the diazo solution containing a further quantity of concentrated hydrochloric acid (10 c.c.). On keeping for an hour in ice the crystalline precipitate was filtered at the pump, washed with hydrochloric acid (*d* 1·2) and than with water till free from acid. The mass was then beaten up with distilled water and caustic soda solution (6 g. in 20 c.c.) was added gradually to it with vigorous mechanical stirring when evolution of nitrogen took place. The whole was then allowed to stand overnight after which the solution was filtered and the residue extracted with a small quantity of boiling water. The combined filtrates were acidified with acetic acid and allowed to settle. The gelatinous precipitate was washed several times with water by decantation after which it was emulsified with water, warmed on the water-bath and a few drops of caustic soda solution were added when the precipitate dissolved. On concentrating the solution on the water-bath the sodium salt began to separate. It was collected, washed with alcohol and obtained as an almost colourless substance not melting up to 300°. (Found: N, 4·32; Sb, 34·82. $C_9H_7O_3NNaSb, H_2O$ requires N, 4·14; Sb, 35·5 per cent).

Sodium quinolyl-8-stibinate was obtained from 8-aminoquinoline, prepared according to Mills and Watson (*J. Chem. Soc.*, 1910, 97, 741); silky needles slightly orange in colour and not melting up to 300°. (Found: N, 3·92; Sb, 36·10. $C_9H_7O_3N\,NaSb, H_2O$ requires N, 4·14; Sb, 35·5 per cent).

Sodium iso*quinolyl-5-stibinate* was prepared from 5-amino*iso*-quinoline in the same way as above in light greyish brown needles not melting up to 300°. (Found: N, 3·85; Sb, 35·18. $C_9H_7O_3N\,Na\,Sb, H_2O$ requires N, 4·14; Sb, 35·5 per cent).

5-Acetoxymercuri-8-oxyquinoline.—An aqueous solution of mercuric acetate (15 g.) acidulated with acetic acid (5 c.c.) was added rapidly with stirring to a solution of 8-oxyquinoline (5 g.) in caustic soda solution (2·5 g. in 250 c. c. of water) when a voluminous precipitate separated. The solution, acid to litmus, was then allowed to stand for an hour after which the supernatant clear liquid was siphoned off. The precipitate was then washed several times with water by decantation, filtered at the pump, washed with water, dried and then washed several times with hot benzene to remove any excess of 8-oxyquinoline. It is a beautiful red powder, decomposing above 280°, insoluble in glacial acetic acid and in alcohol. It is soluble in caustic soda and also in moderately strong hydrochloric acid. (Found: N, 3·05; Hg, 49·1. $C_{11}H_9O_3NHg$ requires N, 3·47; Hg, 49·63 per cent).

7-Acetoxymercuri-5:6-dibromo-8-oxyquinoline was prepared from 5:6-dibromo-8-oxyquinololine as above, the dried product being finally treated several times with hot alcohol to remove dibromo-oxy-quinoline. It is a yellow powder decomposing at 180-81°, insoluble in glacial acetic acid and in common organic solvents, soluble in caustic alkalies which do not decompose it. It is, however, soluble in moderately strong hydrochloric acid. (Found: N, 2·95; Hg, 34·93. $C_{11}H_7O_3NBr_2Hg$ requires N, 2·5; Hg, 35 65 per cent).

7-Acetoxymercuri-5-bromo-8-oxyquinoline was prepared from 5-bromo-8-oxyquinoline. It is a yellow powder decomposing at 231-32°, insoluble in glacial acetic acid and in common organic solvents but soluble in caustic alkali (Found: N, 3·06; Hg, 40·64. $C_{11}H_8O_3NBr\,Hg$ requires N, 2·9; Hg, 41·5 per cent).

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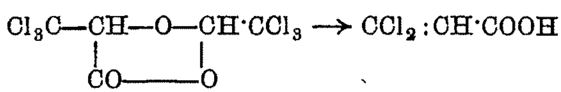
Chloralides from α-Hydroxycarboxylic Acids and their Reduction Products.

By Narshinh Muljibhai Shah and Rupchand Lilaram Alimchandani.

Numerous investigators (Städeler, *Annalen*, 1847, **61**, 101; 1858, **106**, 254 ; Wallach, *ibid.*, 1878, **193**, 1; Otto, *ibid.*, 1888, **239**, 262 ; Kekule, *ibid.*, 1858, **105**, 298 ; Grabousky, *Ber.*, 1873, **6**, 255, 1070 ; 1875, **8**, 1488 ; Schiff, *ibid.*, 1898, **31**, 1898 ; Edeleanu and Zacharia, *Chem. Zentrl.*, 1895, **II**, 212 ; Patterson and Macmillan, *J. Chem. Soc.*, 1912, **101**, 794 ; Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **35**, 1084) have studied the chloralides derived from α-hydroxycarboxylic acids. A solitary instance of reduction of a chloralide by zinc and hydrochloric acid is recorded (Wallach, *loc. cit.*).



In a previous paper (*J. Indian Chem. Soc.*, 1934, **11**, 467) the authors showed that a certain chloralide is reduced with production of a mixed ether in which one of the radicals is derived from the alcohol $HO{\cdot}CH_2{\cdot}CHCl_2$. Because such ethers are hardly known, the authors have prepared the chloralides of malic, tartaric, citric, mandelic and benzilic acids and have reduced them.

Wallach (*loc. cit.*) prepared chloralides by heating the components in sealed tubes and obtained poor yields. The authors have prepared some of them by the method employed by Bhatt (*J. Univ. Bombay*, 1932, **1**, 222) which consists in mixing the acid, chloral hydrate and sulphuric acid. This method, however, proved unsatisfactory with aromatic acids and Wallach's method had to be used.

Benzilic acid chloralide has been obtained for the first time. Some of the other chloralides prepared have different melting points from those recorded by previous investigators (Wallach, *loc. cit.* Bhatt, *loc. cit.* Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 55 ; Yorston, *Rec. trav. chim.*, 1927, **46**, 711). This

difference is due either to the variety of the acid used (racemic or active) or to the method of preparation. The following table shows the melting points of various chloralides recorded by various workers.

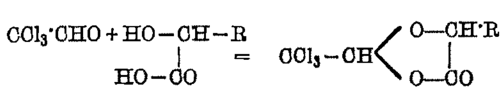
Chloralide of	Wallach.	Bhatt.	Böeseken.	Yorston.	Shah and Alimchandani.
Malic acid	139-40°	139-40°	—	—	180-181°
Tartaric acid	122-24°	128-30°	116-18°	160°	161-62°
	—	156-58°	159-61°	178°	175°
Citric acid	—	161-62°	166°	—	164°
Mandelic acid	82-88°	82-83°	—	—	71°

Previous workers have used *l*-malic acid, whilst the acid used by the authors was optically inactive. Wallach's tartaric acid chloralide differs from that of later workers, because though he started like them with a *d*-tartaric acid, the product obtained by him was inactive owing to racemisation when the acid and chloral were heated together at 150-60° (*cf.* Bhatt, *loc. cit.*). From *d*-tartaric acid, Böeseken obtained two chloralides and Yorston (*loc. cit.*) also got two products. The authors first got Böeseken's product (m.p. 116-18°), which on further crystallisations gave two products (m.p. 161-62° and 175°), which agree with the products of Yorston and as suggested by him, are *cis-trans* isomers. Our citric acid chloralide corresponds with that of previous workers. The mandelic acid that we used was the inactive variety (m.p. 118-19°) ; and on condensation with chloral, it gives a chloralide (m.p. 71°). In spite of repeated crystallisations, we could not get the higher melting point.*

These chloralides on treatment with alkalis decompose giving chloroform, except benzilic acid chloralide which is remarkably stable.

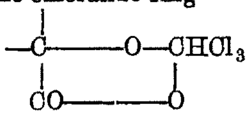
The chloralides have been reduced using zinc dust and acetic acid, the reduction proceeding in a similar manner to that of the group $CH(OH)CCl_3$ (Meldrum and co-workers, *J. Indian Chem. Soc.*, 1925,

* The chloralides

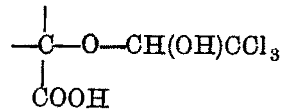


being saturated ring compounds admit of *cis-trans* isomerism ; the radicals CCl_3 and R may be situated on the same side of the ring or on opposite sides. The work on this isomerism is in progress and shall form a future communication. A preliminary note on this isomerism was read in the Chemistry Section of the Indian Science Congress, Bombay, 1934.

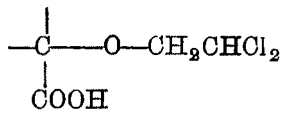
2, 1; 1932, 9, 483; Shah and Alimchandani, *ibid.*, 1931, 8, 262). The chloralide ring



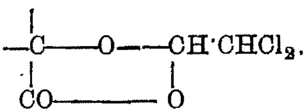
opens and the group



is reduced to the group



in five instances including the one in the preceding paper. Citric acid chloralide is exceptional in that its reduction product contains the group



Both the chloralides of tartaric acid on reduction give identical products.

Saturated formula have been assigned to the reduction products described here because they did not absorb bromine in chloroform or ethereal solution.

These reduction products are stable towards dilute alkalis and can be easily titrated; on heating with sulphuric acid, hydrochloric acid gas is evolved and the substance decomposes.

Experimental

Malic acid chloralide.—Inactive malic acid (Kahlbaum, m. p. 130°, 7 g.) and chloral hydrate (8 g.) were shaken with concentrated sulphuric acid (20 c. c.), when a clear solution was formed which solidified after an hour. The mixture was kept overnight and filtered using flannel and the solid washed and dried It was crystallised from acetic acid and water and finally from hot chloroform as glistening plates, m. p. 180-81°, yield 7·5 g. (Found: Cl, 40·15. $C_6H_5O_5Cl_3$ requires Cl, 40·39 per cent).

Reduction of the malic acid chloralide.—To the suspension of the chloralide (5 g.) in glacial acetic acid (35 c.c.) zinc dust (10-12 g.) was gradually added and after each addition the mixture was shaken. The mixture was shaken for about an hour, when the chloralide dissolved. The filtered solution was neutralised with sodium carbonate and

the calcium salt, prepared by adding calcium chloride to the boiling solution, was decomposed with dilute sulphuric acid, the calcium sulphate removed and the filtrate extracted with ether, dried with sodium sulphate and the ether removed and the solid obtained was crystallised from a mixture of ether and petroleum benzine as rectangular plates, m. p. 130-31°, yield 2 g. (Found: Cl, 30·5; Equiv., 114·9. $C_6H_8O_5Cl_2$ requires Cl, 30·70 per cent. Equiv., 115·5).

Tartaric acid chloralide.—*d*-Tartaric acid (15 g.) and chloral hydrate (33 g.) were shaken with sulphuric acid (60 c.c.) and solid was collected after ½ hour and washed with water. It was crystallised from dilute acetic acid and further purified by dissolving in ether and adding petroleum benzine; prismatic needles, m. p. 161-62°, yield 10 g. On adding more petroleum benzine to the warm mother liquor thin rectangular plates were obtained which were recrystallised from the same solvent as long thin needles, m. p. 170°, yield 4 g. (Found: Cl, 51·75. $C_8H_4O_6Cl_6$ requires Cl, 52·0 per cent).

Reduction of tartaric acid chloralides.—Both the chloralides were separately reduced under similar conditions. Each chloralide (5 g.) was dissolved in acetic acid (25 c.c.) and zinc dust (10 g.) added as described above. The acetic acid filtrate was nearly neutralised with Na_2CO_3 and evaporated to half the bulk, which on acidification with hydrochloric acid gave the reduction product. It crystallised from boiling water as thin light lustrous plates, m. p. 216-17° (decomp.). (Found: Cl, 39·36; Equiv., 182, 180. $C_8H_{10}O_6Cl_4$, H_2O requires Cl, 39·17 per cent. Equiv., 181). The molecule of water could not be removed even on heating to 170° without decomposition.

Citric acid chloralide.—Critic acid (11 g.), chloral hydrate (8 g.) and sulphuric acid (20 c.c.) were mixed, the materials on shaking for about an hour formed a clear solution. After 24 hours, it was poured over ice. The solid was collected, washed with cold water and crystallised from a mixture of glacial acetic acid and concentrated hydrochloric acid, m. p. 164°.

Reduction of citric acid chloralide.—To the hot solution of chloralide (50 g.) in glacial acetic acid (125 c.c.) zinc dust was added as described before. Vigorous reaction took place and the mixture boiled gently. The product was obtained by preparing

the barium salt, which after removing barium as sulphate gave needle shaped crystals on concentration to a small bulk, which were recrystallised from a mixture of ether and petroleum ether as rhombic crystals, m. p. 208°. It crystallised from concentrated hydrochloric acid in clusters of needles. (Found: Cl, 24·84; Equiv., 143·8. $C_8H_8O_7Cl_2$ requires Cl, 24·71 per cent. Equiv., 143·5).

Mandelic acid chloralide.—Inactive mandelic acid (10 g.) and freshly distilled chloral (16 g.) were heated in a sealed tube at 120-25° for about 3 hours. On cooling, the contents were poured into water, a white thick paste separated, which was repeatedly washed with water, when it solidified on keeping. It was first crystallised from dilute acetic acid from petroleum benzine and finally from absolute alcohol as prismatic crystals, m. p. 70-71°. (Found: Cl, 37·83. $C_{10}H_7O_3Cl_3$ requires Cl, 37·82 per cent).

Reduction of mandelic acid chloralide.—The chloralide (6 g.) dissolved in acetic acid (20 c.c.) was reduced as before. The product was precipitated as zinc salt, which on acidification with concentrated hydrochloric acid gave an oil which slowly solidified. It crystallised from benzene as rhombic plates, m. p. 114-15°, yield 3 g. (Found: Cl, 28·56; Equiv., 248·6. $C_{10}H_{10}O_3Cl_2$ requires Cl, 28·47 per cent. Equiv., 248·9).

Benzilic acid chloralide.—Benzilic acid (5 g.) and freshly distilled chloral (8 g.) were heated in a sealed tube for about 5 hours at 160-65°. The contents were poured into water and the oil separating was washed with water when it solidified slowly. It was crystallised from glacial acetic acid and then from absolute alcohol as prismatic needles, m. p. 70°. (Found: Cl, 29·97. $C_{16}H_{11}O_3Cl_3$ requires Cl, 29·77 per cent).

The same chloralide was prepared also by heating the acid and chloral in a flask over a small flame and keeping the molten mixture in contact with concentrated hydrochloric acid in a bottle for 24 hours. This choralide is remarkably stable towards alkaline solutions.

Reduction of benzilic acid chloralide.—To the solution of the chloralide (9 g.) in glacial acetic acid (45 c.c.) zinc dust (15 g.) was added as before. After some time, the mixture solidified; more acid was added and the unchanged zinc removed. The filtrate was neutralised with sodium carbonate and diluted with water when a pasty mass separated; it was washed with water, when it solidified. On crystallising from benzene, a small quantity of a crystalline

product was obtained, m. p. 102-4°. (Found: Cl, 21·61. $C_{16}H_{14}O_3Cl_2$ requires Cl, 21·82 per cent).

The authors are grateful to Late Dr. A. N. Meldrum for his advice and suggestion in connection with this work and to the University of Bombay for a grant to one of them (N. M. S) in aid of this investigation.

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Derivatives of Salicylic Acid. Part VIII. Interaction of Thionyl Chloride with Esters of Hydroxy Aromatic Acids in Presence of Finely Divided Copper. Part III. Synthesis and Constitution of 3:3′-Carbomethoxy-4:4′-hydroxy-5:5′-methyldiphenyl Sulphide and its 6:6′-Methyl Analogue.

By N. W. Hirve, G. V. Jadhav and Y. Chakradeo.

Methyl esters of 3-methyl- and 4-methylsalicylic acids were chosen to continue the work described previously (*J Univ. Bombay*, 1933, 2,128) and it has been found that whereas methyl 5-methylsalicylate does not react, its 3-methyl isomer reacts with difficulty giving a poor yield while the 4-methyl analogue reacts easily giving a good yield.

Though both positions 3 and 5 are favoured by the directing influences of OH and COOH groups in salicylic acid yet the 5-isomer is generally the major product and in sulphonation 5-sulphosalicylic acid alone is obtained. It is interesting to note, in the present investigation, that though the original influence is increased by the presence of the Me group in methyl 4-methylsalicylate, the 5-derivative only is obtained. When the 5-position is occupied by the Me group as in methyl 5-methylsalicylate no condensation could be effected, while in the case of 3-methyl isomer the 5-derivative was obtained with difficulty, indicating that the Me group hinders the directive influences of OH and COOH groups to the position *meta* to itself ; and that the thio group prefers to enter the *para* position to OH group.

As for the mechanism of the reaction it has been found that the presence of copper as a catalyst is necessary, since the reaction is inhibited by the presence of a COOH group. The rôle of copper in the reaction is two-fold. The following series of equations illustrate the reaction :—

(*i*) $3Cu + 4SOCl_2 \longrightarrow 3\,CuCl_2 + S_2Cl_2 + 2SO_2$

(*ii*) $2[C_6H_3(CH_3)(OH)(COOCH_3)] + S_2Cl_2 + Cu \longrightarrow$
$[C_6H_2(CH_3)(OH)(COOCH_3)]_2S + 2HCl + S$

(*iii*) $2CuCl_2 + SO_2 \rightarrow Cu_2Cl_2 + SO_2Cl_2$

(*iv*) $Cu_2Cl_2 + 2SOCl_2 \rightarrow 2CuCl_2 + SCl_2 + SO_2$

(*v*) $2[C_6H_3(CH_3)(OH)(COOCH_3)] + SCl_2 + Cu \text{ or } CuCl_2$
$\rightarrow [C_6H_2(CH_3)(OH)(COOCH_3)]_2S + 2HCl$

Reaction of thionyl chloride with bivalent metals (Mellor, "Treatise of Inorganic Chemistry", Vol. X, 662). supports (*i*). The fact that the sulphur monochloride and sulphur dichloride do not react with the esters without the presence of copper or cuprous chloride, supports (*ii*) and (*v*). That the anhydrous copper chloride does not catalyse the reaction, but it is catalysed by (*a*) the hydrated copper chloride, (*b*) anhydrous copper chloride with traces of water, or (*c*) anhydrous copper chloride with SO_2 initially passed in the mixture, supports equations (*iii*) and (*iv*).

The constitution of the products formed by the action of thionyl chloride on methyl 4-methylsalicylate and methyl 3-methylsalicylate was proved to be 3:3′-carbomethoxy-4:4′-hydroxy-6:6′-methyldiphenyl sulphide and 3:3′-carbomethoxy-4:4′-hydroxy-5:5′-methyldiphenyl sulphide by the action of dilute nitric acid on their respective carboxylic acids, when known 4-methyl-5-nitrosalicylic and 3-methyl-5-nitrosalicylic acids were formed. Concentrated nitric acid, however, reacted with these acids giving 2:4:6-trinitro-3-methylphenol and 4:5:6-trinitro-2-methylphenol.

Experimental.

3:3′-Carbomethoxy-4:4′-hydroxy-6:6′-methyldiphenyl sulphide.— To a mixture of methyl 4-methylsalicylate (30 g.) and thionyl chloride (50 g.) copper dust (20 g.) was gradually added when dense fumes of sulphur dioxide and hydrogen chloride were evolved. The mixture was protected from moisture by fitting the flask with a cork carrying a tube twice bent at right angles and kept at room temperature overnight and then warmed on a water-bath for about an hour. After extracting with chloroform and filtering the copper dust, the filtrate was evaporated and the solid repeatedly crystallised from dilute acetic acid when colourless needles, m. p. 162°, were obtained. It is soluble in chloroform, benzene, acetic acid, carbon disulphide, acetone, ethyl alcohol; insoluble in petroleum ether and carbon tetrachloride and gives bluish violet coloration with ferric chloride solution. (Found: S, 8·87; Equiv, 181·2. $C_{18}H_{18}O_6S$ requires S, 8·84 per cent. Equiv., 181).

The diacetyl derivative, prepared by the action of warm acetic anhydride in presence of a few drops of concentrated sulphuric acid, crystallised from alcohol in colourless needles, m. p. 132°. (Found: S, 7·06. $C_{22}H_{22}O_8S$ requires S, 7·17 per cent).

The dibenzoyl derivative, prepared in pyridine solution and warming the mixture on a water-bath for about 8 hours, crystallised from alcohol in colourless needles, m. p. 140°. (Found: S, 5·48. $C_{32}H_{26}O_8S$ requires S, 5·31 per cent).

The dicarbamido derivative.—A mixture of the carbomethoxy compound (5 g.) and liquor ammonia (100 c. c.) was shaken for about 8 hours and the solid obtained after the evaporation of the liquid was crystallised from glacial acetic acid in gritty flakes, m. p. 280° (decomp.). It is insoluble in alcohol, chloroform, acetone and glacial acetic acid. (Found: N, 8·19 ; S, 9·47. $C_{16}H_{16}O_4N_2S$ requires N, 8 43 ; S, 9·64 per cent).

3 : *3′-Carboxy-4:4′-hydroxy-6:6′-methyldiphenyl sulphide*.—The above ester (10 g.) was treated with sodium hydroxide (10%, 100 c. c.) and boiled for about 2 hours. The solid obtained on acidification with hydrochloric acid was crystallised from glacial acetic acid in colourless plates, m. p. 260° (decomp.). It is difficultly soluble in chloroform and benzene ; insoluble in petroleum ether and soluble in acetone, acetic acid, ethyl alcohol and gives bluish violet coloration with ferric chloride solution. (Found: S, 9·75 ; Equiv., 167·3. $C_{16}H_{14}O_6S$ requires S, 9·58 per cent. Equiv., 167·0).

The diacetyl derivative was prepared in the usual manner, m. p. 199°. (Found: S, 7·53. $C_{20}H_{18}O_8S$ requires, S, 7·65 per cent).

The dibenzoyl derivative crystallised from alcohol in colourless needles, m. p. 188°. It is soluble in common solvents but insoluble in benzene and petroleum ether. (Found: S, 5·79. $C_{30}H_{22}O_8S$ requires S, 5·9 per cent).

The dimethoxy derivative was prepared by methylating with dimethylsulphate and crystallised from alcohol in colourless needles, m. p. 232°. (Found: S, 8·78. $C_{18}H_{18}O_6S$ requires S, 8·84 per cent).

3 : *3′-Carboxy-4:4′-hydroxy-5:5′-bromomethyl-6:6′-diphenyl sulphide*.—The above substance was dissolved in hot glacial acetic acid (200 c. c.) and bromine (5·5 g.) in acetic acid (15 c. c.) was gradually added. The brominated compound which separated on cooling was crystallised from hot glacial acetic acid in colourless needles, m. p. 267° (decomp.). It is insoluble in benzene, petroleum ether;

sparingly soluble in chloroform, ethyl alcohol and acetic acid. (Found: Br, 32·43 ; S, 6·38. Equiv., 245·6. $C_{16}H_{12}O_6Br_2S$ requires Br, 32·52 ; S, 6·50 per cent. Equiv., 246·0).

4-Methyl-5-nitrosalicylic acid.—3 : 3′-Carboxy-4 : 4′-hydroxy-6 : 6′-methyldiphenyl sulphide was suspended in dilute nitric acid (20 c. c. concentrated acid and 80 c. c. water) and warmed till a clear solution was obtained. The solid precipitated on diluting the cold solution with much water was crystallised from dilute alcohol, m. p. 219°. (Found: N, 6·93. $C_8H_7O_5N$ requires N, 7·11 per cent). Borsche and Berkhout (*Annalen*, 1903, **330**, 100) give m. p. 219°.

2 : 4 : 6-*Trinitro-3-methylphenol.*—When the original thioether (1 g.) was treated with concentrated nitric acid (10 c.c.) warmed a little and then diluted with water a solid compound was obtained which crystallised from alcohol, m. p. 108°. (Found: N, 16·96. $C_7H_5O_7N_3$ requires N, 17·28 per cent). Nölting and Salis (*Ber.*, 1881, **14**, 987) give m. p. 105-6°.

3 : 3′-*Carbomethoxy-4 : 4′-hydroxy-5 : 5′-methyldiphenyl sulphide.*—This was prepared from methyl 3-methylsalicylate (30 g.) thionyl chloride (50 g.) and copper dust (20 g.) and isolated like its 6-methyl isomer ; but in this case a pasty solid was obtained which was washed with petroleum ether and repeatedly crystallised from dilute acid in needles, m. p. 161°. It resembles its 6-methyl isomer in solubility and other properties. (Found: S, 8·8. Equiv., 182·3. $C_{18}H_{18}O_6S$ requires S, 18·84 per cent. Equiv., 181·0).

3 : 3′-*Carboxy-4 : 4′-hydroxy-5 : 5′-methyldiphenyl sulphide.*—It was obtained by hydrolysing the above ester with sodium hydroxide (10%, 100 c. c.). It crystallised from glacial acetic acid in colourless plates, m. p. 279° (decomp.). It resembles its 6-methyl isomer in solubility and other properties. (Found: S, 9·5; Equiv, 167·2. $C_{16}H_{14}O_6S$ requires S, 9·6 per cent. Equiv., 167·0). It gave 3-methyl-5-nitro-salicylic acid with dilute nitric acid. It crystallised from dilute alcohol in needles, m. p. 199°. (Found: N, 6·9, $C_8H_7O_5N$ requires N, 7·11 per cent). (Einhorn and Pfyl, *Annalen*, 1900, **311**, 47 ; Borsche and Berkhout, *loc. cit.*) give m. p. 199°). Concentrated nitric acid gave 4 : 5 : 6-trinitro-2-methyl-phenol, m. p. 102°. (Found: N, 17·0. $C_7H_5O_7N_3$ requires N, 17·28 per cent) Nölting and Collin (*Ber.*, 1884, **17**, 270) and Sommer (*J. pr. Chem.*, 1903, *ii*, **67**, 553) give m. p. 102°.

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Studies in the Coagulation of Colloids. Part VIII. The Viscosity Changes in Colloid Arsenious Sulphide when Coagulated by Binary Mixtures of Potassium Halides in the Slow Region.

By Shridhar Sarvottam Joshi and T. R. Gopalaswami Iyengar.

The earliest observations of the effect of electrolytes on the viscosity of colloidal solutions were made by Gokun (*Z Chem. Ind. Kolloide*, 1908, **3**, 84), who showed that the rate of increase of the viscosity with time of pure gelatine solutions is diminished by the addition of ammonium nitrate. Schorr (*Biochem. Z.*, 1908, **13**, 173), Pauli and Handovsky (*ibid* , 1909, **18**, 340), and Woudstra (*Z. Chem. Ind. Kolloide*, 1911, **8**, 73) studied η, the viscosity of colloidal solutions as a function of c, the concentration of the added electrolyte. The chief result of these investigations is that the η-c relation is not a simple one, a *minimum* being usually observed in the early part of the curve. Dhar and co-workers (*J. Phys. Chem.*, 1926, **30**, 1646; *Kolloid Z.*, 1928, **44**, 225 ; 1929, **48**, 43) have confirmed this in the case of a number of colloidal solutions.

It would appear, however, that despite the investigations of Kawamura (*J. Coll. Sci. Imp. Univ. Tokyo*, 1908, **25**, No. 8), Freundlich and Ishizaka (*Trans. Faraday Soc.*, 1913, **9**, 66), Wo. Ostwald (*ibid.*, p. 34), Pauli (*ibid.*, p. 64), Smoluchowski (*Kolloid Z.*, 1916, **18**, 190), and especially Gann (*Koll. Chem. Beih.*, 1916, **8**, 65), detailed information is not available on the time variation of the viscosity of a colloid of the *lyophobe* type when treated with an electrolyte solution.

Work carried out in these laboratories (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329; Joshi and Menon, *ibid.*, 1933, **10**, 599; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133) has shown that in the *slow* region, the coagulation is not a time-continuous process unless viscosity change is not always an index of the corresponding

coagulation. It has been observed that the η-time curve is discontinuous and that a diminution of η, soon after the start of coagulation is usually produced. In view of the obvious bearing of these facts on our views on the kinetics of coagulation it was of interest to examine the above phenomena under conditions different from those used previously (*loc. cit.*). In the present work mixtures of KF, KCl, KBr and KI in different proportions have been used as the coagulating agents. It might also be added that practically no information is available in the literature on the viscosity variations produced in colloids when coagulated by electrolyte mixtures. Observations with the fluoride have been made in some detail in view of the marked paucity in the literature of coagulation data made with this coagulant.

Experimental.

The arsenious sulphide sol used in these experiments was prepared by adding intermittently small quantities of a triturated solution of arsenious oxide to a saturated solution of hydrogen sulphide in water. The excess of H_2S was removed by passing a current of hydrogen. The colloid content of the sol, thus prepared, was estimated by coagulating a known volume of the sol with a suitable electrolyte and after washing the coagulum free of the electrolyte, drying it at 200° and weighing. Thus determined, the colloid content was 10·7 g. per litre. The viscosity of the colloid mixed with an equal volume of a solution of any one or more of the alkali halides in suitable proportions was determined by the Scarpa's method with appropriate modifications as described by Joshi and Menon (*loc. cit.*). The results are expressed relative to the viscosity of water taken as unity. The temperature of the thermostat was kept constant at 35° ± 0·1 in all the experiments. The suction applied was regulated within 0·2 mm. at 26 cms. of water. The condition of the apparatus to give reproducible results was repeatedly examined by measuring the viscosity of water at different times during the course of these experiments. The accuracy of measurements with water was never found to be less than 0·15. Changes exceeding by *at least* three times the last quantity only have been reported. The viscometer was well illuminated by a light behind the thermostat. During every observation the colloid in the viscometer and that in the outside jar containing the viscometer was very carefully exa-

mined for the slightest appearance of flocculation, *i.e.*, of fine particles of the coagulum produced either in the liquid, or left on the walls of the viscometer. When this was observed η-measurements were discontinued.

In curves 1—45 (Figs. 1—4) abscissa stands for the time axis and ordinates for η. In order to prevent overlapping of curves in a given series and especially to economise space, a number of curves have been drawn with separate time and η-axis. The scale units chosen are indicated in the figure with reference to the curve or curves to which they correspond. The composition of the coagulating mixture corresponding to the η-time curves in a vertical row is shown in a tabular form preceding the diagrams (*cf.* Table II).

The data given in Table I were deduced from curves in Fgs. 1—4. The normalities in the coagulating mixture of each one of the four electrolytes used are indicated in the second column, the third gives the total halide content in the mixture. The fourth and fifth columns represent η_i, the initial and η_m, the first minimum viscosity. The difference between these quantities has been expressed as a percentage of the initial viscosity and results shown under η_d, in the sixth column. To give an idea of the discontinuities of the η-time curves, η_a the lowest viscosity observed in 2 hours (except in cases when coagulation with deposition of particles occured earlier as in coagulations represented by curves 2, 4 in Fig. 1; 15, 18 in Fig. 2; 25, 27, 44 in Fig.3 and 32 in Fig. 4) is shown in column 8, *e g.*, $a=$ 1·005 in curve 14, Fig. 2, η_b, the highest viscosity reached in the same period is given in column 9, *e.g.*, $b=1{\cdot}027$, in the same curve. The difference between these two, *viz.*, 0·022 is expressed as a percentage, *viz.*, 2·18 of η_i, the initial viscosity, 1·088, and the results quoted in column 10, under R. $T\eta_m$ indicates the time in minutes corresponding to η_m, the first minimum on the η-time curve.

TABLE I.

1	2							3	4	5	6	7	8	9	10
Curve No.	Normality of electrolytes in the system. KCl.		KBr.		KI,		KF.	Total halide normality.	η_i.	η_m.	η_d.	T_{η_m}.	η_s.	η_b.	R.
1	0·03125	+	Nil	+	Nil	+	Nil	0·03125	1·034	1·015	1·84	19	1·015	1·020	0·48
2	0·05000	+	,,	+	,,	+	,,	0·05000	1·047	1·041	—	9	1·041	—	—
3	Nil	+	0·03125	+	,,	+	,,	0.03125	1·030	1·008	2·14	32	1·007	1·018	0·60
4	,,	+	0·05000	+	,,	+	,,	0·05000	1·026	—	—	—	—	—	—
5	,,	+	,,	+	0·03125	+	,,	0 03125	1·033	1·016	1·65	32	1·012	1·019	0·68
6	,,	+	,,	+	0·05000	+	,,	0·05000	1·040	1·015	2·40	43	1·015	1·022	0·67
7	,,	+	,,	+	Nil	+	0·03125	0·03125	1·029	1·004	2·43	24	1·003	1·014	1·07
8	,,	+	,,	+	,,	+	0·05000	0·05000	1·030	1·007	2·23	25	1·002	1·009	0·68
9	,,	+	,,	+	,,	+	0·06250	0·06250	1·021	1·002	1·86	33	1·002	1·007	0·49
10	,,	+	,,	+	,,	+	0·07500	0·07500	1·013	1·000	1·28	18	1·000	1·007	0·69
11	,,	+	,,	+	,,	+	0·08750	0·08750	1·006	0·9880	1·80	34	0·9879	0·9936	0·57
12	,,	+	,,	+	,,	+	0·12500	0·12500	0·9995	0·9788	2·07	23	0·9777	0·9847	0·70
13	,,	+	0·02500	+	0·00625	+	Nil	0·03125	1·028	1·004	2·34	24	1·002	1·009	0·68
14	,,	+	0·00625	+	0·02500	+	,,	0·03125	1·033	1·005	2·71	36	1·005	1·027	2·13
15	,,	+	0·02500	+	0·02500	+	,,	0·05000	1·035	1·019	1·55	17	1·019	—	—

16	0·02500	+	0·00625	+	Nil	+	,,	0·03125	1·028	1·009	1·85	42	1·007	1·013	0·58
17	0·00625	+	0·02500	+	,,	+	,,	0·03125	1·019	1·006	1·28	24	1·005	1·010	0·50
18	0·02500	+	0·02500	+	,,	+	,,	0·05000	1·047	—	—	—	—	—	—
19	0·02500	+	Nil	+	0·00625	+	,,	0·03125	1·006	0·9951	1·0	17	0·9951	1·004	0·89
20	0·00625	+	,,	+	0·02500	+	,,	0·03125	1·035	1·015	1·93	40	1·015	1·019	—
21	0·02500	+	,,	+	0·02500	+	,,	0·05000	1·024	1·000	1·86	32	1·000	1·012	1·17
22	0·00625	+	,,	+	Nil	+	0·02500	0·03125	1·006	0·9752	3·06	17	0·9752	0·9897	1·44
23	0·02500	+	,,	+	,,	+	0·00625	0·03125	0·9974	0·9716	2·59	17	0·9716	0·9783	0·67
24	0·02500	+	,,	+	,,	+	0·02500	0·05000	0·9845	0·9670	1·78	16	0·9627	0·9721	0·96
25	0·03750	+	,,	+	,,	+	0·03750	0·07500	0·9991	0·9897	0·84	9	0·9897	—	—
26	0·02500	+	,,	+	,,	+	0·07500	0·10000	0·9940	0·9743	1·98	17	0·9743	0·9954	2·12
27	0·02500	+	,,	+	,,	+	0·10000	0·12500	0·9974	—	—	—	—	—	—
28	0·01250	+	,,	+	,,	+	0·05000	0·06250	0·9886	0·9714	1·74	24	0·9672	0·9849	1·79
29	Nil	+	,,	+	0·00625	+	0·02500	0·03125	0·9902	0·9727	1·77	17	0·9709	0·9763	0·55
30	,,	+	,,	+	0·02500	+	0·00625	0·03125	0·9995	0·9747	2·50	17	0·9712	0·9772	0·60
31	,,	+	,,	+	0·02500	+	0·02500	0·05000	0·9959	0·9656	3·04	27	0·9656	0·9721	0·65
32	,,	+	,,	+	0·03750	+	0·03750	0·07500	0·9974	0·9779	1·95	17	0·9779	—	—
33	,,	+	,,	+	0·02500	+	0·05000	0·07500	0·9870	0·9665	2·08	33	0·9645	0·9727	0·83
34	,,	+	,,	+	0·02500	+	0·07500	0·10000	0·9951	0·9766	1·86	32	0·9766	0·9885	0·69
35	,,	+	,,	+	0·02500	+	0·010000	0·12500	0·9954	0·9822	1·83	17	0·9822	0·9991	1·70

1			2					3	4	5	6	7	8	9	10
Curve No.	Normality of electrolytes in the system							Total halide normality	η_c	η_m	η_d	$T\eta_m$	η_a	η_b	R
	KCl		KBr		KI		KF								
36	,,	+	,,	+	0·01250	+	0·05000	006250	0··9854	0·9757	0·98	25	0·9738	0·9772	—
37	,,	+	0·00625	+	Nil	+	0·02500	0·03125	0·9837	0·9607	2·40	17	0·9561	0 9632	0·72
38	,,	+	0·02500	+	,,	+	0·00625	0·031 25	0·9919	0·9605	3·17	17	0·9592	0·9665	0·74
39	,,	+	0·02500	+	,,	+	0·02500	0·5000	0·9595	0·9612	2·86	16	0·9596	0·9642	—
40	,,	+	0·03750	+	,,	+	0·03750	0·07500	0·9838	0·9642	1·94	26	0·9642	0·9863	2·25
41	,,	+	0·02500	+	,,	+	0·05000	0·07500	0·9900	0·9610	2·98	16	0·9598	0·9658	0·61
42	,,	+	0·02500	+	,,	+	0·07500	0·10000	0·9902	0·9672	2·32	16	0·9672	—	—
43	,,	+	0·02500	+	,,	+	0·10000	0·12500	0·9763	0·9736	0·28	32	0·9736	0·9874	1·41
44	,,	+	0·05000	+	,,	+	0·01250	0·06250	1·005	0·9917	1·32	8	0·9917	—	—
45	,,	+	0·01250	+	,,	+	0·05000	0·06250	0·9900	0·9645	2·58	24	0·9601	0.9661	0·61

TABLE II.

For the elucidation of the curves in Figs. 1—4, consult the following table.

(FIG. 1)

Curve			
1	20 c.c. sol + 1·25 c.c.	N-KCl	+ 18·75 c.c. water
2	+ 2·00	,,	+ 18·00
3	+ 1·25	N-KBr	+ 18·75
4	+ 2·00	,,	+ 18·00
5	+ 1·25	N-KI	+ 18·75
6	+ 2·00	,,	+ 18·00
7	+ 1·25	N-KF	+ 18·75
8	+ 2·00	,,	+ 18·00
9	+ 2·50	,,	+ 17·50
10	+ 3·00	,,	+ 17·00
11	+ 3·50	,,	+ 16·50
12	+ 5·00	,,	+ 15·00

(FIG. 2)

Curve			
16	20 c.c. sol + 1·00 c.c. N-KCl	+ 0·25 c.c. N-KBr	+ 18·75 c.c. water
17	+ 0·25	+ 1·00	+ 18·75
18	+ 1·00	+ 1·00	+ 18·00
13	20 c.c. sol + 1·00 c.c. N-KBr	+ 0·25 c.c. N-KI	+ 18·75 c.c. water
14	+ 0·25	+ 1·00	+ 18·75
15	+ 1·00	+ 1·00	+ 18·00

(FIG. 3)

Curve			
19	20 c.c. sol + 1·00 c.c. N-KCl	+ 0·25 c.c. N-KI	+ 18·75 c.c. water
20	+ 0·25	+ 1·00	+ 18·75
21	+ 1·00	+ 1·00	+ 18·00
37	+ 1·00 N-KF	+ 0·25 N-KBr	+ 18·75
38	+ 0·25	+ 1·00	+ 18·75
44	+ 0·50	+ 2·00	+ 17·50
22	+ 1·00	+ 0·25 N-KCl	+ 18·75
23	+ 0·25	+ 1·00	+ 18·75
24	+ 1·00	+ 1·00	+ 18·00
25	+ 1·50	+ 1·50	+ 17·00
26	+ 3·00	+ 1·00	+ 16·00
27	+ 4·00	+ 1·00	+ 15·00
28	+ 2·00	+ 0·50	+ 17·50

(FIG. 4)

Curve 29	20 c.c. sol + 1·00 c.c. *N*-KF	+ 0·25 c.c. *N*-KI	+ 18·75 c.c. water
30	+ 0·25	+ 1·00	+ 18·75
31	+ 1·00	+ 1·00	+ 18·00
32	+ 1·50	+ 1·50	+ 17·00
33	+ 2·00	+ 1·00	+ 17·00
34	+ 3·00	+ 1·00	+ 16·00
35	+ 4·00	+ 1·00	+ 15·00

Curve 36	20 c.c. sol + 2·00 c.c. *N*-KF	+ 0·50 c.c. *N*-KI	+ 17·50 c.c. water
39	+ 1·00	+ 1·00 *N*-KBr	+ 18·00
40	+ 1·50	+ 1·50	+ 17·00
41	+ 2·00	+ 1·00	+ 17·00
42	+ 3·00	+ 1·00	+ 16·00
43	+ 4·00	+ 1·00	+ 15·00
45	+ 2·00	+ 0·50	+ 17·50

TABLE III.

Influence on η_m by 20% change of composition.

Total halide conc. = 0·03125*N*

Cl	Br	I	F
1·84	1·85	1·08	2·59
Br	Cl	I	F
2·14	1·28	2·34	3·17
I	Cl	Br	F
1·65	1·93	2·71	2·50
F	Cl	Br	I
2·48	1·85	2·40	1·77

TABLE IV.

Influence on η_m by 50% change of composition.

Total halide conc. = 0·05*N*.

Cl	Br	I	F
0·57	—	1·86	1·78
Br	Cl	I	F
—	—	1·55	2·86
I	Cl	Br	F
2·40	1·86	1·55	3·04
F	Cl	Br	I
2·28	1·78	2·86	3·04

Fig. 1.

Sol+KCl ; KI ; KF.

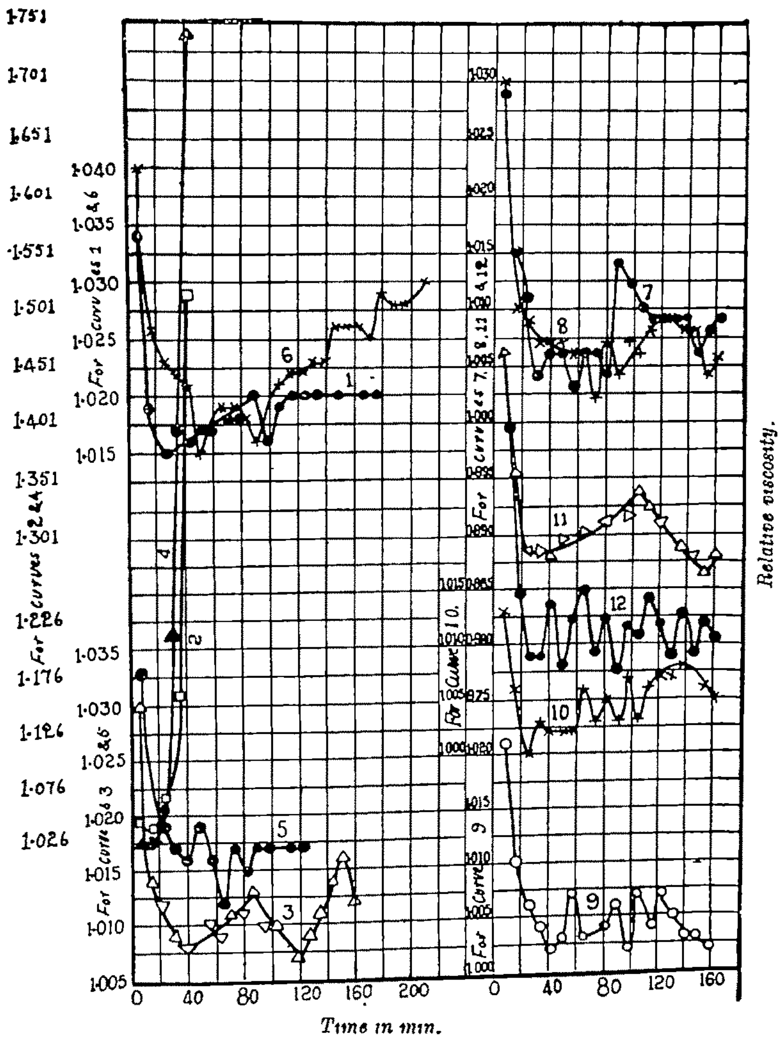


FIG. 2.

Sol+KBr ; *Sol*+KCl+KBr.

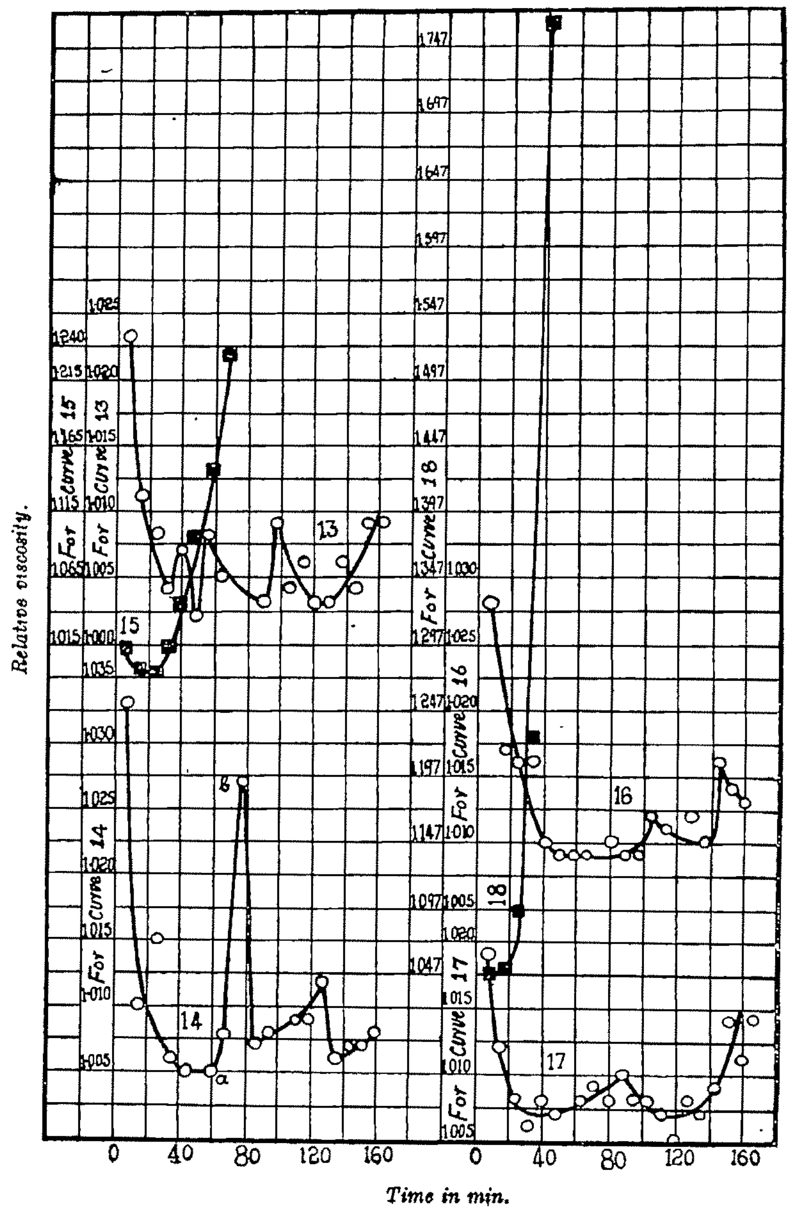


FIG. 3.

Sol+KCl+KI ; *Sol*+KF+KBr.

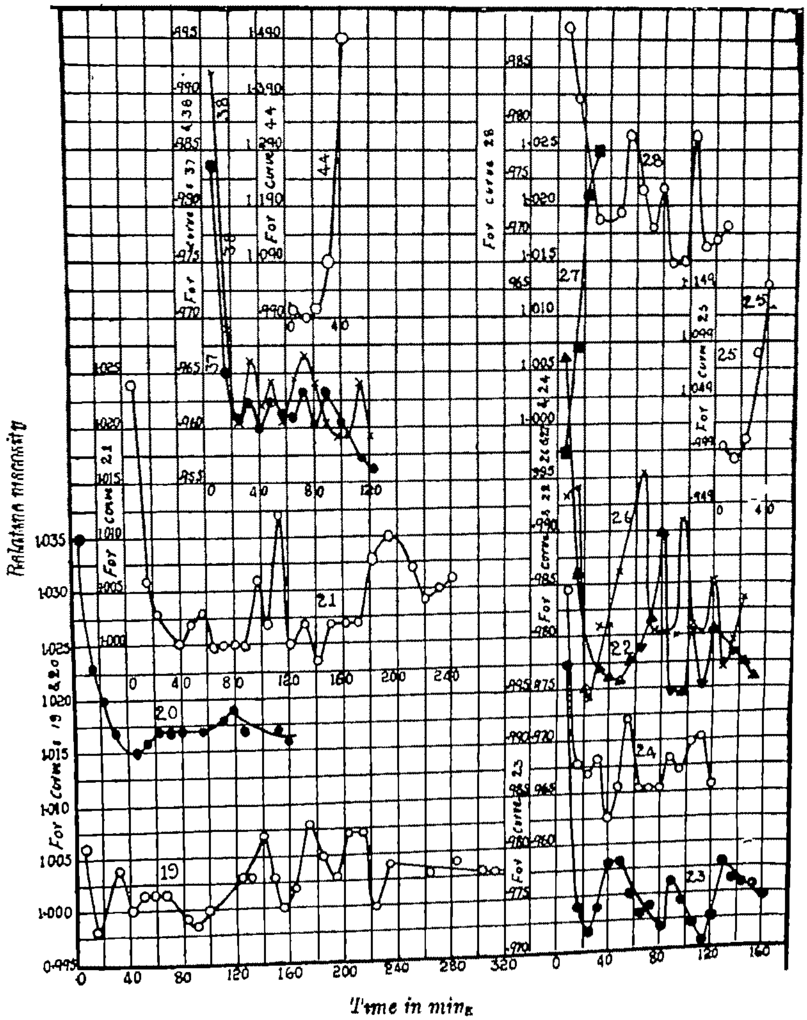
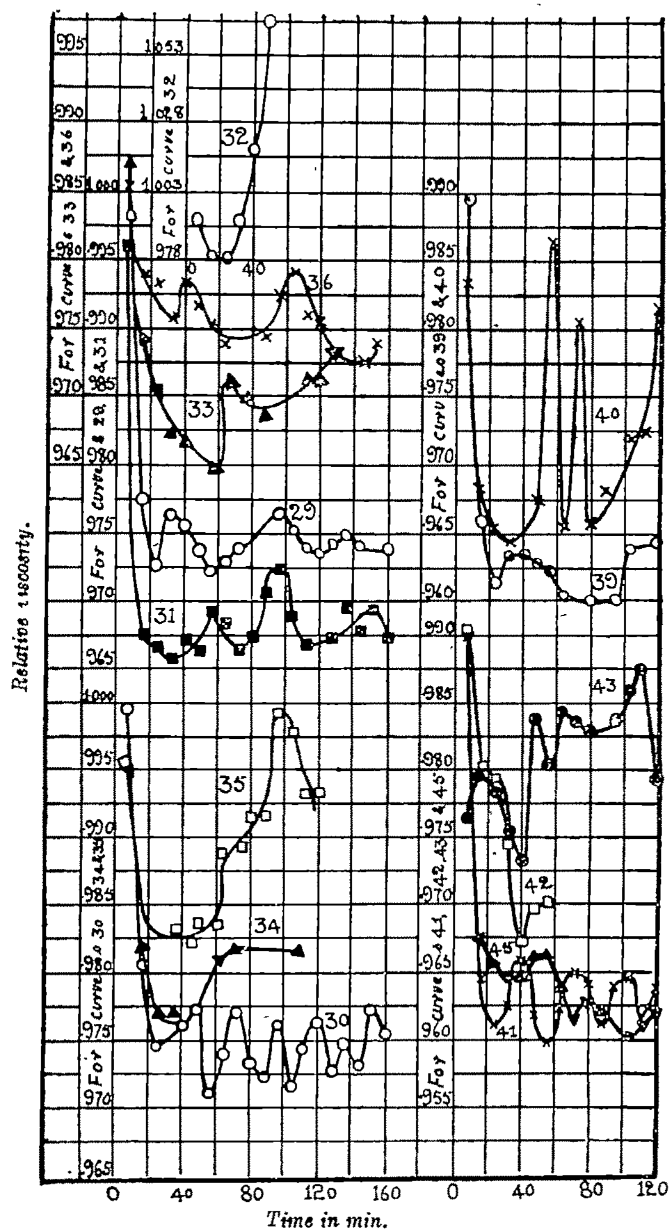


FIG. 4

Sol+KF+KI ; *Sol*+KF+KBr.



DISCUSSION.

It is now well known that Smoluchowski's theory (*Z. physikal. Chem.*, 1917, **92**, 129) for the kinetics of coagulation breaks down for *slow* coagulations. The mechanism of the coagulation process as contemplated in this theory is that, coagulation is but a *continued* coalescence of the original colloid particles to form bigger aggregates. The change is, therefore, considered as progressing continuously during the coagulation-time. On this basis, therefore, it is to be anticipated that a colloid-sensitive property like viscosity, would vary continuously during the coagulation. The η-time curves in Figs. 1—4 show, however, that distinctly the contrary is the case at any rate in the *slow* region. It is seen from column 10 in Table I that the breaks in these curves vary in the range 0·5 to 2% of the initial viscosity. It is considered that this is appreciably greater than the probable experimental error. Now it is probable for instance starting with a certain number of primaries (by which is meant simply the original particles of the sol) when mixed with the coagulator, the formation of agglomerates through successive coalescence might obtain as the main process during a certain period, and that during this period the viscosity might vary in a certain sense, *e.g.*, increase. After this period depending upon the stage of the coalscence, the agglomerate might suffer a break down due (*i*) either to instability induced as a result of the charge on the size and the nature of the structure of the sol particles reached, or (*ii*) by the action of the ions carrying the same charge as the sol. This will produce a viscosity change in a direction opposite to what happened previously. When examined over a prolonged time, the operation of the two sets of factors mentioned above will produce breaks on the η-time curve, as observed. A considerable amount of evidence has now been accumulated in these laboratories on the existence of these breaks by using other properties besides viscosity to measure coagulation, which will be published shortly.

It is not unlikely that the occurrence of the initial viscosity fall observed in a very large number of coagulations reported already (*loc. cit.*) is distinctive of some early stage in the process of coagulation. In the present work this quantity varies in the range 0·5 to 4% of the initial viscosity (column). It is significant that $T\eta_m$, the time corresponding to the attainment of η_m, the minimum viscosity varies in the range 16 to 40 minutes in 40 out of 45 coagulations examined, when both the nature and the concentration of the coagulator were varied over a markedly wide range. It is known that but small

changes in c, the electrolyte concentration produce very marked changes in T, the time corresponding to the attainment of a given stage of coagulation as is for example illusirated by Paine's well known exponential relation for c and T (*Koll. Chem Beih.*, 1912, **16**, 430). It is to be noted that $T\eta_m$ the time required for attaining the first minimum viscosity is not influenced markedly by alterations in c. Presently therefore, it correspends to some change which is of a different nature from that represented by T.

It is instructive to examine the magnitude of the initial fall in η and the discontinuousness of the η-time curves in relation to the composition of the coagulating mixture. The amount of colloid was constant; except when potassium flouride was used, (curves 7-12, Fig. 1; 22-28, Fig. 3 and 29-45, Fig. 4) that of any of the other halides, or of the binary mixture was generally increased up to 2 c.c. N. With this maximum amount of the coagulating substance, the η-time curves show a *continuous* rapid rise (*cf.* curves 2, 4, 15, 18, 25, 27, 32, 42 and 44). The initial fall occurs in 6 out of these 9 coagulations and varies in the range 0·8 to 2%; its absence in the remaining three coagulations (curves 4, 18 and 27) might be due to the viscosity rising rapidly to large values from the very start of the coagulation, and thus marking the comparatively smaller changes in the initial stages. Precisely similar results under above conditions have been reported in previous publications (*loc. cit.*).

η-time curves for coagulations with the flouride show a comparatively large initial fall and subsequent discontinuities, although its amount in the coagulating mixture was increased to 5 c.c.N (curves 7-12, Fig. 1). For less than half this normality, curves for KCl and KBr rise rapidly and continuously (*cf.* curves 2 and 4, Fig. 1). The influence of KI appears to be intermediate between KF on the one hand and KCl and KBr on the other. Thus for example, for 2 c.c. of N-KI, the η-time curve (No. 6, Fig. 1) has a greater initial fall, is slower rising, and more discontinuous than those when the same normality of KCl and KBr was added (curves 2 and 4, Fig. 1). A rapid rising and continuous curve is obtained only when 0·5 c.c. of N-KCl is added to 2 c.c. of N-KI (No. 44, Fig. 3). An interesting comparison of the relative influences of these halides is obtained by examining the following curves:

Curve 12, Fig. 1 refers to coagulation by 5 c.c. of N-KF only; it shows first a large fall of viscosity, *vis.*, 2·07% in the

ntial stage; then, on the whole, the viscosity tends to diminish during coagulation, and that markedly *discontinuously*. When the above amonut of KF is replaced partly by KI, that is, when the coagulant is 4 c.c. N-KF+1c.c. of N-KI, the η-time curve (No. 35, Fig. 4) shows a smaller initial fall, *viz.*, 1 38% and the viscosity increases almost up to the initial value; as in the previous case the curves consist of a number of breaks. Now, with 4 c.c. of N-KF and 1 c.c. N-KBr (curve 43, Fig. 4) there is no initial fall, but the viscosity rises comparatively rapidly though discontinuously. When 1 c.c. N-KCl is substituted for KBr that is with 4 c.c. N-KF+ I c.c. N-KBr, the curve has no initial fall and is markedly steep and continuous (No. 27, Fig. 3). An examination of curves 7-12, Fig. 1 shows that although the amount of KF is increased five fold, the η-time curve shows an appreciable initial fall, is discontinuous and the viscosity does not rise beyond the initial value.

From an examination of the results in Table I for η_m (which denotes the percentage diminution of viscosity in the initial stage) the results in Tables III and IV would appear to be deducible. For the same halide normality, the initial fall is greater with potassium fluoride than with potassium chloride, the influence of the bromide and the iodide being intermediate. This is clear from the data for the initial fall quoted in the first vertical column of Tables III and IV in which the normality of any *one* of the halides used, *viz.*, KCl, KBr, KI and KF was 0·03125 and 0·050 respectively. The data in the other vertical columns show the influence of substituting for the halide in the first vertical column by that mentioned in the subsequent columns.

Thus for example considering the first horizontal row in Table III, η_m due to 0·03125N-KCl *only* is 1·84%. It is 1·85 when the coagulation is due to 0·02500N-KCl mixed with 0·00625 KBr (*cf.* curve 16). This result shows, therefore, the infiuenee of substituting KCl by 25% KBr. In precisely the same way, by comparing the results for a mixture of KCl and KF (*cf.* curve 28) with that obtained when only KCl was used, the influence on η_m of substituting 25% of KCl by KF is obtained. The data in the second horizontal row show the influence on η_m of substituting 25% KBr by KCl, KI and KF. Table IV records similar results when the total halide concentration was higher, *viz.*, 0·05N. These results show that η_m increases by introducing KF in the halide mixture used as a coagulant. Conversely it is seen that η_m diminishes when KF is partly or wholly displaced by any of the other halides.

In an attempt to correlate the above differences in the influences of the halides with some of their characteristic properties, the viscosity of their aqueous solutions would appear to be the first to suggest itself. For the order of the concentrations of the halides used in the present experiments, *viz.*, $N/8$ to $N/20$, the viscosities of solutions appear to be practically the same as that of water (*cf.* Landolt-Bornstein, 1923, Erster Band, pp. 160-61). At higher concentrations, however, the order is KI<KBr<KCl<KF, the effect of KF in increasing η being very markedly greater than that of any of the other three halides. The second factor to be considered is the concentration of the ions derived from the dissociation of each of the above halides. This is sufficiently indicated by their equivalent conductivities (corrected for the viscosity). The order deduced from known data for the above quantity for the concentrations used here (*loc. cit.*, Zweiter Band, p. 1079) is KF<KCl<KI<KBr. The conductivity of the last three is approximately the same, while that of KF is markedly lower. The failure to get a rapid rising η-time curve with KF using concentrations more than twice that of any other halide might, therefore, be ascribed in part to its lower ionisation. One more factor to be considered in this connection and which very probably involves the two other mentioned above, is the coagulative power. This is largely determined by the adsorbability of coagulator by the colloid, and therefore depends upon the nature of the latter. In the absence of relevant data, however, the case of colloid ferric oxide might be considered. The order is KI<KBr<KCl (*cf.* Freundlich, "Colloid and Capillary Chemistry," 1926, p. 421). The colloid power for the iodide being markedly less than those of the other two which are similar. This is in agreement with their influence on the viscosity change during coagulation as discussed already.

It would appear to be almost a tacit assumption with colloid chemists that viscosity increases as a result of coagulation. Work now in progress in these laboratories shows, however, that this assumption is not warranted (Joshi and Nanjappa, *J. Indian Chem. Soc.*, 1934, **11**, 133). This is also seen from the η-time curves in Figs. 1—4. In at least 30 out of the 45 coagulations examined, the viscosity does not rise beyond the initial value during quite an appreciable time. This together with the finding of discontinuities on the η-time curves would appear to invalidate the use of viscosity as a measure of coagulation at any rate in the *slow* region.

SUMMARY.

1. The progress of coagulation in the *slow* region of the arsenious sulphide sol by solutions of KCl, KBr, KI and KF, and also of their mixtures in different proportions have been examined by measurement of η, the viscosity by Scarpa's method.

2. It has been found that (*a*) the coagulation does not progress continuously with time, but occurs in a number of discontinuous stages marked by breaks on the η-time curves, and (*b*) that usually the first stage of the change is marked by a diminution of viscosity in the range 0·5 to 4% of the initial value. Both these features disappear in rapid coagulations. The initial viscosity diminution and the discontinuousness of the η-time curve have been found to increase by increasing the proportion of KF in the mixture of potassium halides used as a coagulant.

3. It has been also observed in a number of coagulatives that during quite an appreciable period of time, *viz.*, about two hours after the start of the coagulation the viscosity of the mixture does not increase beyond the initial value.

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Studies in the Coagulation of Colloids Part IX. The Effect of Stirring on the Time Variation of Viscosity of Colloid Arsenic and Antimony Sulphides when Coagulated by Simple Electrolytes in the Slow Region.

By Shridhar Sarvottam Joshi and T. R. Gopalaswami Iyengar.

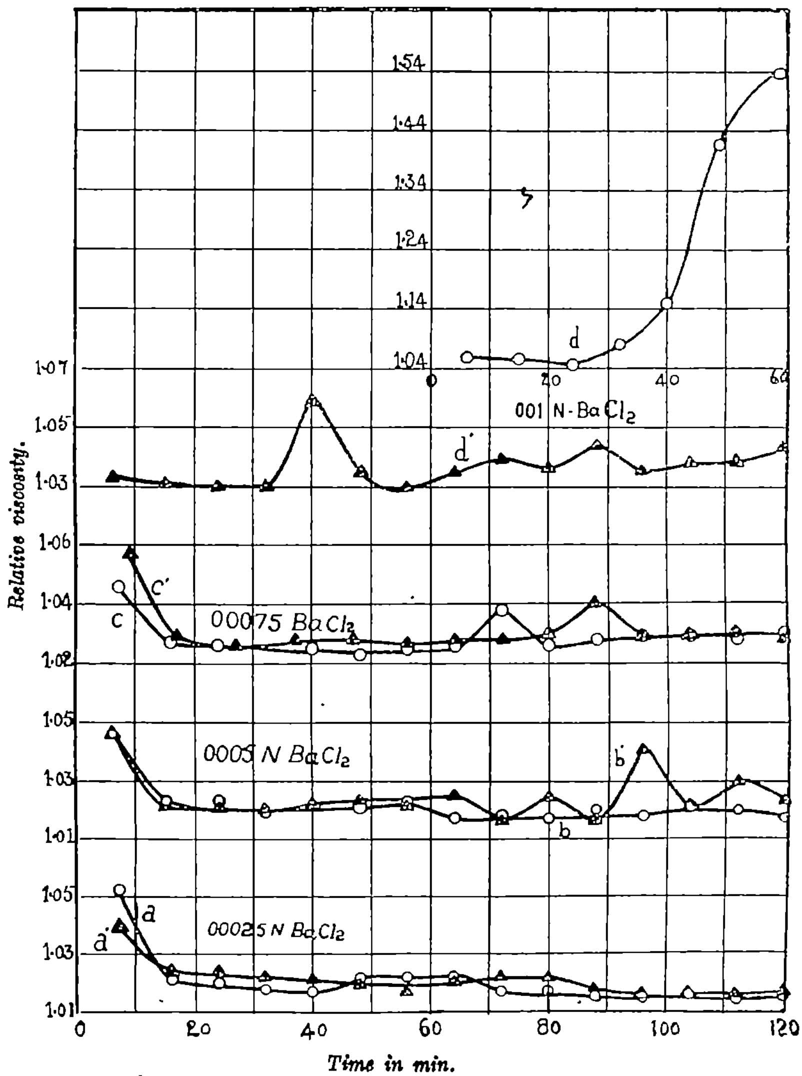
The following experiments were carried out in continuation of the work on the kinetics of the coagulation of colloids for some time in progress in these laboratories (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329 ; Joshi and Menon, *ibid.*, 1933, **10**, 600; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133). It is found that the progress of coagulation in the *slow* region followed by measuring η, the viscosity of the coagulating sol, was marked by (*a*) discontinuities on η-time curves, and (*b*) usually though not invariably by a fall in η during the initial stages of coagulation. It is well known that one of the respects in which a colloid differs markedly from a molecular system is the possible influence on the former of such mechanical and allied conditions as the age of the sol, the mode of introducing the coagulating solution, its flow through a capillary, shaking, etc. It was sought in previous work (*loc. cit.*) to keep these factors constant by adhering as far as practicable to a constant experimental procedure. For instance, the last of the factors mentioned above was kept constant by giving twice a rotatory motion to the mixture immediately after mixing. In view of the claims made by some workers (*vide infra*) that stirring has an appreciable influence on the rate of coagulation, it was considered desirable to make systematic experiments to estimate this factor, especially with a view to investigate if the course of a coagulation is appreciably changed by stirring,- in respect of the two features observed previously, *viz*, (*a*) and (*b*).

Experimental.

The arsenious sulphide sol used in experiments *a*—*g'* in Figs. 1, and 2 was prepared by adding intermittently small quantities of a triturated solution of arsenious oxide to a saturated solution of hydrogen sulphide in water. The excess of H_2S was removed by passing a current of hydrogen. The antimony sulphide sol (*cf.* curves *h*—*m'*, Fig. 3) was prepared as recommended by Joshi and Prabhu (*ibid.*, 1931, **8**, 11). It was dialysed for 12 days against repeated changes

FIG 1.

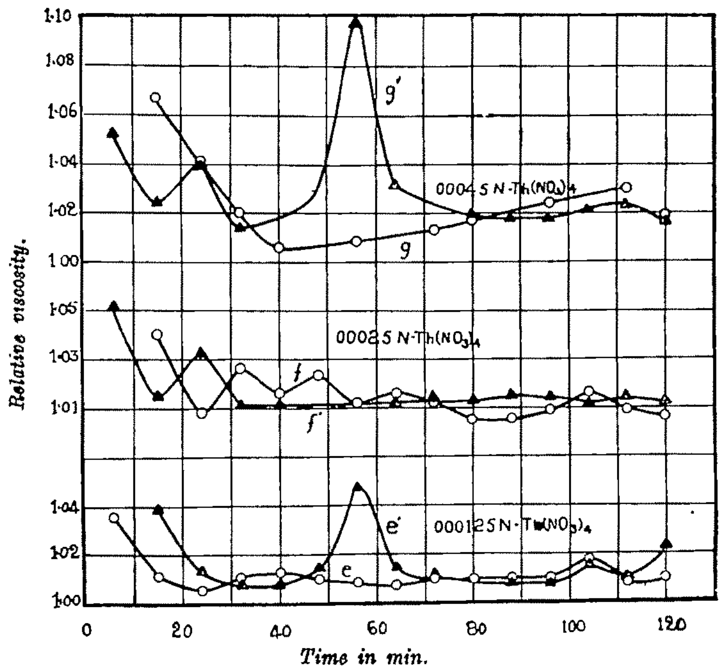
As_2S_3 *Sol.*



of hot water and was found free of acid. The concentrations of both sols were determined by coagulating a known volume and weighing the dried coagulam (previously washed free of coagulator). The sol contents were 10·7 and 2·05 g. of As_2S_3 and Sb_2S_3 per litre respectively.

FIG 2.

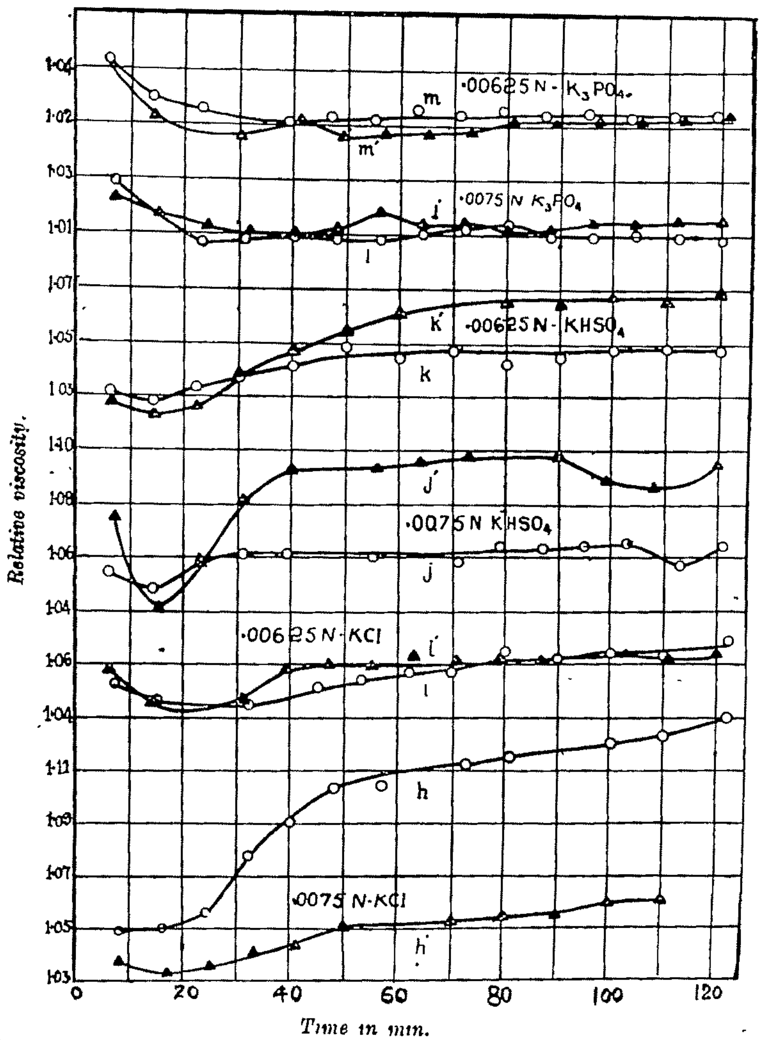
As_2S_3 *Sol.*



The measurements of viscosity were made by Scarpa's method with modifications described previously (Joshi and Viswanath, *loc. cit.*). The temperature of the thermostat was maintained constant at $35 \pm 0{\cdot}1°$. The suction applied was $26 \pm 0{\cdot}05$ cm. in all the experiments. The other precautions and details of experimental procedure have been described in previous papers. The constant k of the instrument was found by observation of the times of rise and fall for water. η is expressed relative to that of water taken equal to unity. In order to study the effect of stirring, η-time observations were made with coagulating mixtures under as far as possible identical conditions with and without stirring. A hand regulated glass stirrer operating vertically and giving 30 strokes per minute was used. The stirring of the mixture was started 1·5 minutes before taking every η-observation, and continued for one minute. These η-time observations taken with and without stirring have been shown graphically by curves a', b', c',...m' and a, b, c,...m respectively in Fig. 1-3. The coagulators used were differently concentrated solutions of KCl,

FIG 8.

Sb_2S_3 *Sol.*



$KHSO_4$, K_3PO_4, $BaCl_2$ and $Th(NO_3)_4$. In order to prevent overlapping of the curves and also economise space, *pairs* of η-time curves in a given series of coagulations have been shown in the same figure using different origins. The units for the time and scale are the same in all the curves.

DISCUSSION.

An examination of the foregoing curves shows that the influence of stirring on the variation of η, the viscosity of a coagulating sol is not appreciable at small concentrations of the coagulator. This is in agreement with the results of Freundlich and Basu (*Z. physikal. Chem.*, 1925, **115**, 203), and of Freundlich and Kroch (*ibid.*, 1926, **124**, 155) who have found that vigorous stirring causes coagulation, and moderate stirring has but small effect in the presence of low amounts of the electrolyte. Freundlich and co-workers (*loc. cit.*; *ibid.*, 1928, **139**, 368) also find that stirring accelerates coagulation at higher concentrations of the electrolytes provided they are absorbed strongly by the colloid; definite exceptions to this deduction were, however, noted in some cases when stirring appeared to retard coagulation. In the present experiments the mixture was stirred only for a short time before each measurements of viscosity. The last mentioned finding of Freundlich and co-workers applies in part to the present results in the sense that greater the electrolyte concentration, the greater is the divergence between the η-time curves for coagulation with and without stirring (Fig. 1, *cf.* curves *dd'*; Fig. 3, *hh'*, *jj'*). It is also interesting to point out that with large concentrations of KCl and $BaCl_2$ the effect of stirring is to cause a general lowering of viscosity. The opposite, however, is the case with $KHSO_4$ (*cf.* Fig. 3, curves *jj'*, *kk'*). Whether this implies a like influence on the rate of coagulation is not certain in view of the results published already (*loc. cit.*) that a viscosity change might not necessarily be a measure of corresponding coagulation produced at any rate in the *slow* region. It was observed previously (*cf.* Joshi and Menon, *loc. cit.*) that the η-variations show pronounced discontinuities when Th $(NO_3)_4$ is used as a coagulant. This obtains in coagulations now studied with and without stirring (*cf.* Fig. 2).

These results also show that in by far the majority of cases the effect of stirring is sensible only after the initial stages of coagulation. It is also of interest to observe that the occurrence of discontinuities on η-time curves, and of the fall of viscosity during the *initial* stages persist even after the stirring of the mixture, and that the magnitude of the last quantity is approximately constant.

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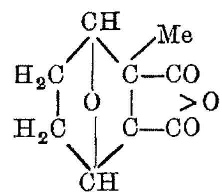
Page.	*line.*	*for*	*Read*
84	4*	heated	treated
86	10*	b. p. 90°-92°	b. p. 90°-92°/42 mm
199	1	b. p 80·5−110°	b. p. 80−5−110°
231		formula (I).	
265	4	centeed	centred
411	7*	with acetic acid	with acetic anhydride
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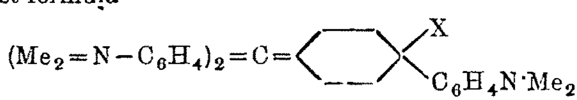


* From bottom.

Studies in Optical Rotation. Rotatory Powers of Acidyl-biscamphorquinonehydrazones and Camphorylthiocarbamylhydrazides and Attempts to Prepare Compounds Possessing Abnormal Rotation.

By M. S. Kotnis, B. Sanjiva Rao and P. C. Guha.

Section A.

In an attempt to correlate the effect of chemical constitution with optical rotatory power, Frankland (*J. Chem. Soc.*, 1912, **101**, 654) has observed that molecular rotation of a homologous series changes gradually until a maximum is reached and then declines or remains constant. Hilditch (*J. Chem. Soc.*, 1909, **95**, 1578) found that in the menthyl esters of the aliphatic dibasic acids, there is a decrease of rotation in passing from the first to the second and after that an increase up to the fifth (adipic); whereas, in the case of the brucine salts the value goes on increasing up to the third and from there decreases *via* fourth up to the fifth (Table I). The anomalous rotation of the oxalic acid derivatives, particularly in the brucine salt series, is probably due to the contiguity of two carboxylic groups. Evidently, Hilditch's results are not in conformity with Frankland's observation and hence it seemed desirable to follow up the study of the dibasic acids further.

As the menthyl esters and the brucine salts of these acids have been examined by Hilditch (*loc. cit.*), it seemed desirable to study an entirely different class of derivatives of these acids and compare the results with those obtained by him. Besides the camphorquinone derivative of the five hydrazides—oxalic to adipic, three more *viz.*, those of carbo-, *tere*phthalic and *iso*phthalic have also been prepared for the sake of comparison. Table I gives the values of $[\alpha]_{5893}$ and $[M]_{5893}$ for $2\frac{1}{2}$ and 5% solutions of the menthyl esters and brucine salts as observed by Hilditch while the values for $[\alpha]$ and $[M]$ now obtained for acidylcamphorquinonehydrazones with both green and yellow mercury lines, are given in Table II.

TABLE I.

Acid.	*l*-Menthyl esters 2·5% $[\alpha]_D$.	2·5% $[M]_D$.	5·0% $[\alpha]_D$.	5·0% $[M]_D$.	Brucine salts 5·0% $[\alpha]_D$.	5·0% $[M]_D$.	2·5% $[\alpha]_D$.	2·5% $[M]_D$.
Oxalic	−103·4	−378·4	−104·0	−380·6	3·0	26·3	2·8	24·6
Malonic	−79·54	−302·6	−79·24	−301·1	52·76	470·6	52·76	470·6
Succinic	−82·40	−324·6	−81·90	−322·7	65·30	591·6	64·12	580·9
Glutaric	−80·16	−327·1	−80·26	−329·3	50·62	465·8	50·40	464·4
Adipic	−83·60	−352·8	−83·80	−353·6	42·80	399·2	42·60	397·8

TABLE II.

Camphorquinone hydrazones.	M. p.	$[\alpha]_y$.	$[M]_y$.	$[\alpha]_g$.	$[M]_g$.	Disp. coeff. $[M]_g/[M]_y$.
Carbo	22·5°	286·6	1106	334·4	1290	1·17
Oxalic	249	256·1	1060	298·6	1237	1·18
Malonic	185	251·3	1075	272·1	1165	1·08
Succinic	275	—	—	—	—	—
Glutaric	219	213·7	970·3	261·2	1186	1·22
Adipic	220	195·4	914·7	260·7	1220	1·33

FIG. 1.

Sp. Rotations of acidyl biscamphorquinone-hydrazones.

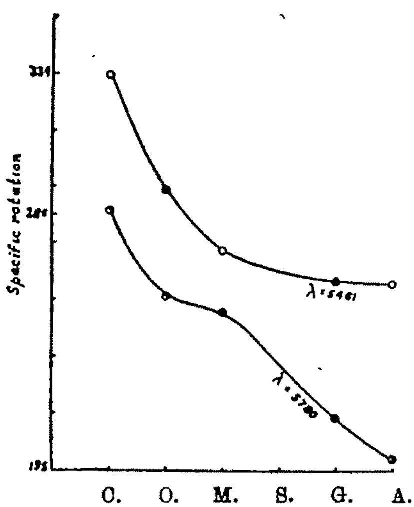
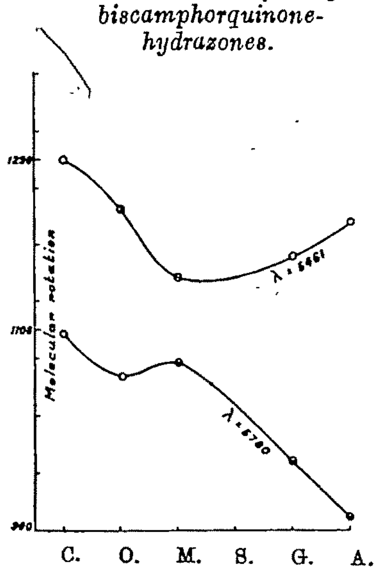


FIG. 2.

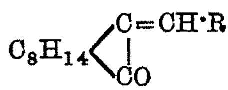
Mol. Rotations of acidyl biscamphorquinone-hydrazones.



It will be observed from Table II as well as from Fig. 1 that the specific rotations of the different substances fall sharply from carbo-biscamphorquinonehydrazone to the corresponding oxalic compound

and then gradually decrease along the series. This is rather contrary to Hilditch's observation of a second maximum with the adipic compound. Coming to the molecular rotation, however, the case is not so simple (*cf.* Fig. 2), because the malonic compound has a higher molecular rotation than the oxalic for the yellow light. Similarly, the glutaric derivative just exceeds the corresponding malonic compound in its molecular rotation for the green light. It was rather unfortunate that the succinic hydrazide should have yielded an insoluble compound, its rotation thus remaining unascertained; the general fall in the specific as well as molecular rotation is, however, quite distinct. The molecular rotations as observed in this series go to support Frankland's view.

The dispersion coefficient varies between 1·08 and 1·33. The use of these data for the calculation of the dispersion curves of optically active compounds of a homologous series has been recorded by Hagenback (*Z. physikal. Chem.*, 1915, **89**, 570). The constancy of the coefficient of dispersive power was observed also by Rupe (*Annalen*, 1915, **409**, 327) who obtained $\alpha_F/\alpha_c = 2·31$ for methylenecamphors of the type



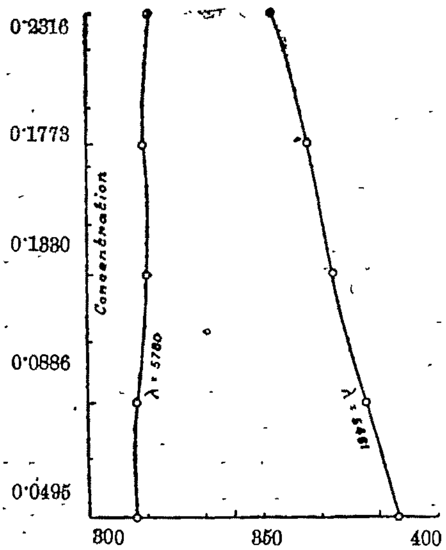
In order to determine the effect of concentration on the specific rotation and rotatory dispersion, the rotation of carbonyl-biscamphorquinonehydrazone under various concentrations have been studied. The choice of the carbohydrazide derivative for this purpose is only due to its yielding fairly soluble compounds with both camphorquinone and camphoryl mustard oil.

TABLE III.

Effect of concentration on the rotation of carbonyl-biscamphorquinonehydrazone.

G. in 100 c.c.	$[\alpha]_y$.	$[M]_y$.	$[\alpha]_g$.	$[M]_g$.	Dispn. coeff. $[\alpha]_g/[\alpha]_y$
0·0495	316·0	1220	406·2	1568	1·29
0·0886	316·0	1220	395·0	1525	1·25
0·1330	319·6	1234	383·6	1480	1·20
0·1773	318·8	1230	375·2	1448	1·18
0·2216	320·4	1237	363·4	1403	1·13

FIG. 3.

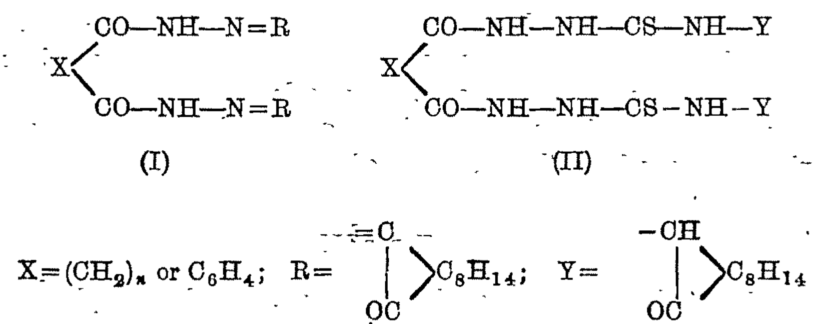


Change of specific rotation with concentration. Carbonyl-biscamphorquinonehydrazone in alcohol.

From Table III it will be observed that the specific rotation gradually drops with increasing concentration for the green light (Fig. 3), with the yellow light it is, however, fairly constant.

Section B.

In section A, the various observations made about the optical rotatory power of camphorquinonehydrazones (I) of the dibasic acids have been described. In this part, it is proposed to take up another set of compounds *viz.*, the camphorylthiocarbamyl hydrazides (II) of the same acids.



As there are two sulphur atoms attached to two carbon atoms in the chain between the camphor and the dibasic acid residue it was expected to exert some influence on the rotatory power of these compounds. A study of the optical rotatory powers of compounds of this series and a comparison with those already obtained for the corresponding camphorquinonehydrazones has, therefore, been made.

TABLE IV.

Biscamphorylthiocarbamylhydrazides.

Biscamphoryl-thiocarbamyl hydrazides	M. p.	$[\alpha]_y$	$[M]_y$	$[\alpha]_g$	$[M]_g$	Dispn. coeff. $[M]_g/[M]_y$
Carbo	208°	28·2	143·2	32·9	167·1	1·17
Oxalic	245	30·4	162·9	50·7	271·7	1·67
Malonic	185	29·8	163·9	50·7	278·9	1·70
Succinic	275	39·7	224·0	50·5	284·8	1·27
Glutaric	201	12·4	71·7	18·6	107·5	1·50
Adipic	207	33·4	197·7	42·4	251·0	1·27

FIG. 4.

Specific rotation of biscamphorylthiocarbamylhydrazides.

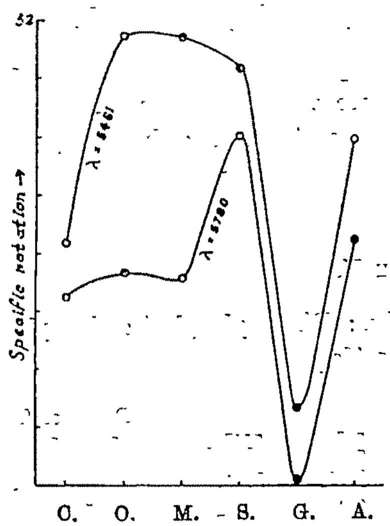


FIG. 5.

Molecular rotation of biscamphorylthiocarbamylhydrazides.

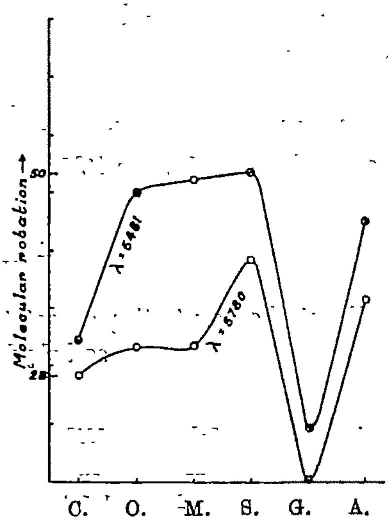


Table IV gives the values for the specific and molecular rotations as well as rotatory dispersion and dispersion coefficients of these

compounds. The first point that strikes one is the lower rotatory powers of these compounds compared with those of the camphorquinonehydrazones. This is not peculiar to these series of compounds alone, it being well known that introduction of a sulphur atom in the camphor derivatives generally lowers the rotatory power of the compound to a very great extent (*J. Chem. Soc.*, 1905, **87**, 115; 1907, **91**, 1886; *J. Ind. Inst. Sci.*, 1927, **10A**, 88). As seen from Fig. 4, the specific rotation curve of these compounds is anything but regular. For the yellow light, the curve rises a little from the carbo to the oxalic hydrazide but again declines to a slight extent for the malonic compound. The specific rotation then jumps up in the case of the succinic followed by a steep decline for the glutaric hydrazide. Finally with the adipic compound the curve again rises up, the specific rotation assuming a value in the neighbourhood of those for the first two members of the series. This alternation is also observed in the case of the melting points of these hydrazides. With the green light, however, the specific rotation rises steeply from carbo to oxalic and is practically constant for oxalic, malonic and succinic compounds though the rest of the curve runs parallel to that for the yellow light. The curves for the molecular rotation (Fig. 5) are more or less similar to those for the specific rotation for the corresponding light. Thus it will be seen that the curves for the specific or molecular rotation of the biscamphorylthiocarbamylhydrazides show practically no similarity with those of the corresponding camphorquinonehydrazones. This can be attributed mainly to the presence of sulphur atoms in the compound. The values for the dispersion coefficient for the compounds fluctuate between 1·70 to 1·27.

TABLE V.

Effect of concentration on rotation: Biscamphorylthiocarbamylcarbohydrazide.

G. in 100 c.c.	$[\alpha]_y$.	$[M]_y$.	$[\alpha]_g$.	$[M]_g$.	Dispn. coeff. $[\alpha]_g/[\alpha]_y$.
0·0425	—	—	23·5	119·4	
0·0850	21·2	107·6	27·4	139·2	1·15
0·1275	24·7	125·5	28·6	145·3	1·16
0·1700	26·4	134·2	30·2	153·4	1·14
0·2125	28·2	142·7	32·9	166·5	1·17

Table V contains the values obtained for the specific rotation of biscamphorylthiocarbamylcarbohydrazide with solutions of various concentrations. The curves for the same (Fig. 6) run practically parallel to one another. Moreover, the rotation increases with concentration in agreement with Hilditch's observation *viz.*, the specific rotations of the menthyl esters and brucine salts of the oxalic acid series are greater for a 5% solution than for a 2·5% solution. This forms another point of contrast between the camphorquinonehydrazones and camphorylthiocarbamylhydrazides (*cf.* Fig. 8). Coming to the question of the dispersion coefficient it will be observed that it is practically constant for the solutions of all concentrations. As the solutions of camphorylidenecarbohydrazide reveal the same fact, it might be safely deduced that the dispersion coefficient has a constant value for any particular compound.

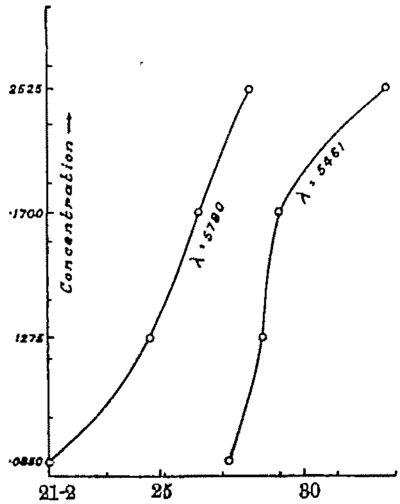


FIG. 6.

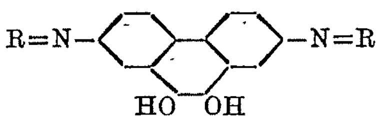
Change of specific rotation with concentration of biscamphorylthiocarbamylcarbohydrazide in alcohol.

Section C.

In this laboratory, Patel and Guha (*J. Indian Chem. Soc.*, 1934, **11**, 87) have prepared 1:4-naphthylenebisiminobenzylidene-iminocamphor containing 17 double bonds and having $[M]_D = 22000°$. It was sought to extend the work further by preparing a few more compounds likely to possess high molecular rotation. The following compounds, *viz.*, (*a*) camphorquinonehydrazone of benzaldeyde-*p*-iminocamphor, (*b*) *tere*phthaldiamido-bis-phenylene-4 : 4-iminocamphor, (*c*) 9:10-phenanthraquinol-2:7-bisiminocamphor, (*d*) camphoriminonaphthalene-4-azo-*p*-camphoriminobenzene, (*e*) 1:1′-dinaphthylurea-4:4′-bisiminocamphor, possessing all or most of the characteristics required for abnormal rotation (*cf.* Forster and Spinner, *J. Chem. Soc.*, 1919, **115**, 889) were expected to show high molecular rotation.

$R{=}N{-}N{=}CH{-}C_6H_4{-}N{=}R \qquad \left(R= \begin{matrix}:C\\ |\\ OC\end{matrix}\!\!>C_8H_{14}\right)$ ... (a)

$R{:}N{-}C_6H_4{-}NH{-}CO{-}C_6H_4{-}CO{-}NH{-}C_6H_4{-}N{:}R$ ... (b)


... ... (c)

$R{=}N{-}C_{10}H_6{-}N{=}N{-}C_6H_4{-}N{:}R$ ... ... (d)

$CO(NH{\cdot}C_{10}H_6{\cdot}N{:}R)_2$ ... ... (e)

Difficulties were encountered in the preparation of most of these compounds. The preparation of (*a*) from *p*-camphoryliminobenzaldehyde or from camphorylhydrazone of *p*-aminobenzaldehyde was not possible as neither camphorquinone nor its hydrazone condensed with *p*-aminobenzaldehyde due perhaps to the latter being polymerised (Walther and Mausch, *J. pr. Chem.*, 1897, **56**, 102). The hydrolysis of the acetyl group of *p*-acetaminobenzylidene camphorquinonehydrazone (I), prepared as follows:

$$R{=}N{-}NH_2 + OCH{\cdot}C_6H_4{\cdot}NHAc \longrightarrow R{=}N{-}N{=}CH{\cdot}C_6H_4{\cdot}NHAc \quad (I)$$

could not be effected with dilute alkali, *p*-acetaminobenzaldehyde and camphor being obtained; with dilute acids, the products being azocamphanone and *p*-aminobenzaldehyde.

The preparation of the diamine by de-acetylating *tere*phthalylbis-*p*-acetphenylenediamine (II) was not possible as during de-acetylation the molecule broke up into *tere*phthalic acid and *p*-phenylenediamine. Attempts to reduce *tere*phthalyldi-*p*-nitroaniline (III) or di-*p*-azobenzene-*tere*phthalyldiamide (IV) to obtain the same amine also failed.

2:7-Diamino-9:10-phenanthraquinol required for compound (*c*) was prepared according to Kessman and Wense (*Ber.*, 1885, **18**, 2169) but neither this nor aminonaphthalene-4-azo-*p*-aminobenzene required for the preparation of (*d*) could be condensed with camphorquinone.

The hydrochloride of *pp*-diaminodinaphthylurea (VI) obtained by reduction of the corresponding dinitro compound (V) which was in its turn obtained by condensing 1:4-nitronaphthylamine with phenyl carbonate, gave with potassium cyanate, the expected dicarbamido-

dinaphthylurea (VII). The condensation of the hydrochloride with camphorquinone, though tried under varying conditions of experiments, gave only a brownish tarry resinous mass from which the resinous compouud (*e*) could not be isolated.

$$C_6H_4(CO{\cdot}NH{\cdot}C_6H_4{\cdot}NHAc)_2 \quad \text{(II)} \qquad C_6H_4(CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)_2 \quad \text{(III)}$$

$$C_6H_4(CO{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}NPh)_2 \quad \text{(IV)} \qquad CO(NH{\cdot}C_{10}H_6{\cdot}NO_2)_2 \quad \text{(V)}$$

$$CO(NH{\cdot}C_{10}H_6{\cdot}NH_2)_2 \quad \text{(VI)} \qquad CO(NH{\cdot}C_{10}H_6{\cdot}NH{\cdot}CONH_2)_2 \quad \text{(VII)}$$

EXPERIMENTAL.

Section A.

The dihydrazides of oxalic, malonic, succinic, glutaric, adipic, *terep*hthalic and *iso*phthalic acids were prepared by the action of hydrazine hydrate on their ethyl esters. Carbohydrazide was prepared by the action of hydrazine hydrate on phenylcarbonate (Cazeneuve and Moreau, *Compt. rend.*, 1899, **129**, 1255). The camphorquinone compounds of the dihydrazides were readily obtained by heating concentrated aqueous solution of the former with an alcoholic solution of the latter on a water-bath for 2-4 hours. The camphorylidene hydrazides are generally pale yellow compounds, sparingly soluble in alcohol, much less soluble in other organic solvents.

sym*Carbobiscamphorquinonehydrazone* (R : N·NH·CO·NH·N : R).—Carbohydrazide (1·5 g., 1 mol.) was dissolved in water (5 c.c.) and mixed with a solution of camphorquinone (5·5 g., 2 mol.) in alcohol (25 c.c.) and the mixture heated on a water-bath for 4 hours. The precipitate obtained on dilution with water was crystallised from 50% alcohol in pale yellow needles, m.p. 225°, yield 3 g. (43%). (Found: N, 14·7. $C_{21}H_{30}O_3N_4$ requires N, 14·51 per cent). 0·1047 G. of the substance dissolved in 50 c.c. of 95% alcohol gave a rotation of 1·2 (yellow) and 1·40 (green) in a 2 dcm. tube. Hence $[\alpha]_y = 286{\cdot}6°$ and $[\alpha]_g = 334{\cdot}4°$ and $[M]_y = 1106$, $[M]_g = 1290$.

sym*Oxalyl-biscamphorquinonehydrazone* (R : N–NH–CO–CO–NH–N=R).—Oxalylhydrazide (2 g., 1 mol.), dissolved in a little water, was added to a solution of camphorquinone (5·6 g., 2 mol.) in alcohol. The pale yellow precipitate formed on heating the mixture

for 2 hours was recrystallised from alcohol, m.p. 249°, yield 5·5 g. (72%). (Found: N, 13·26. $C_{22}H_{30}O_4N_4$ requires N, 13·5 per cent). 0·1172 G. of the substance in 50 c.c. alcohol showed a rotation of 1·2° (yellow), 1·4° (green) in a 2 dcm. tube. Hence $[\alpha]_y = 256{\cdot}1°$, $[\alpha]_g = 298{\cdot}6°$ and $[M]_y = 1060°$, $[M]_g = 1237$.

Malonyl-biscamphorquinonehydrazone (I, X = CH_2).—Malonic hydrazide (2·0 g.) and camphorquinone (5·0 g.) gave a pale yellow powder (4 g. or 57%), m.p. 185°. (Found: N, 13·4. $C_{23}H_{32}O_4N_4$ requires N, 13·08 per cent). 0·1194 G. of the substance in 50 c.c. alcohol showed a rotation of 1·2° (yellow) and 1·3° (green) in a 2 dcm. tube; hence $[\alpha]_y = 251{\cdot}3$, $[\alpha]_g = 272{\cdot}1$ and $[M]_y = 1075$, $[M]_g = 1165$.

Succinyl-biscamphorquinonehydrazone [I, X = $(CH_2)_2$]—Succinic hydrazide (2 g.) and camphorquinone (4 6 g.) gave 5·5 g. (90%) of a product which was very sparingly soluble in all organic solvents. It was purified by washing with water and boiling alcohol, m.p. 275°. (Found: N, 12·83. $C_{24}H_{34}O_4N_4$ requires N, 12·7 per cent). As the substance is very difficultly soluble, its optical rotation could not be determined.

Glutaryl-biscamphorquinonehydrazone [I, X = $(CH_2)_3$].—Glutaric hydrazide (2 g.) and camphorquinone (4·1 g.) yielded 4 g. (67%) of the product which recrystallised from alcohol, m.p. 219°. (Found: N, 12·1. $C_{25}H_{36}O_4N_4$ requires N, 12·28 per cent). 0·1053G. of the substance showed a rotation of 0·90° and 1·1° for yellow and green light respectively in a 2 dcm. tube and 50 c.c. alcohol; hence $[\alpha]_y = 213{\cdot}7$, $[\alpha]_g = 261{\cdot}2$ and $[M]_y = 970{\cdot}3$, $[M]_g = 1186$.

Adipyl-biscamphorquinonehydrazone [I, X = $(CH_2)_4$] obtained in 60% yield from adipic hydrazide (1 mol.) and camphorquinone (2 mol.) recrystallised from dilute alcohol, m.p. 220°. (Found: N, 11·8. $C_{26}H_{36}O_4N_4$ requires N, 11·91 per cent). 0·1151 G. of the substance dissolved in 50 c.c. alcohol showed in a 2 dcm. tube a rotation of 0·94° and 1·2° for yellow and green light respectively. Hence $[\alpha]_y = 195{\cdot}4$, $[\alpha]_g = 260{\cdot}7$ and $[M]_y = 914{\cdot}7$, $[M]_g = 1220$.

Tere*phthalyl-biscamphorquinonehydrazone* (I, X = C_6H_4) was prepared from *tere*phthalic hydrazide and camphorquinone, m.p. 279°. (Found: N, 11·59. $C_{28}H_{34}O_4N_4$ requires N, 11·43 per cent). The substance being insoluble, its rotatory power could not be determined.

iso*Phthalyl-biscamphorquinonehydrazone* melted at 274° after repeatedly boiling with alcohol and water. The rotation could not be determined owing to the sparing solubility of the substance.

Section B.

Camphorylthiocarbamylhydrazides obtained from camphoryl mustard oil and the hydrazides as white precipitates are generally mixed up with some unreacted camphoryl mustard oil from which they could not be easily freed by crystallisation. The best method, is, however, to dissolve these products in a little alcohol and precipitate fractionally by water, the highest melting fractions after one or two crystallisations giving the pure product. They are all very sparingly soluble in solvents like benzene, chloroform, etc. but are fairly soluble in alcohol which furnished a good medium for optical measurements. The specific rotations are much lower than those of the corresponding camphorquinonehydrazones.

Carbonyl-biscamphorylthiocarbamylhydrazide [CO(NH·NH·CS·NH·Y)$_2$].—A mixture of carbohydrazide (1 mol.) dissolved in a little water and camphorylthiocarbimide (2 mol.) dissolved in alcohol was heated on a water-bath for 4 hours. The precipitate obtained on cooling melted at 155° while the mother liquor yielded on dilution with water a precipitate which was crystallised from alcohol in silvery plates, m.p. 208°. (Found: N, 16·13. $C_{23}H_{36}O_3N_6S_2$ requires N, 16·54 per cent). $[\alpha]_y=28·2$, $[\alpha]_g=32·9$ and $[M]_y=148·2$, $[M]_g=167·1$.)

Oxalyl-biscamphorylthiocarbamylhydrazide CO·NH·NH·CS·NH·Y
|
CO·NH·NH·CS·NH·Y

The precipitate obtained from the reaction mixture on cooling and diluting with a little water melted at 231°, the mother liquor yielding on further dilution, a precipitate, m.p. 200-05°. The first fraction was recrystallised from boiling alcohol in silvery plates, m.p. 245°. It is sparingly soluble in alcohol. (Found: N, 15·8. $C_{24}H_{36}O_4N_6S_2$ requires N, 15·7 per cent). $[\alpha]_y=30·4$, $[\alpha]_g=50·7$ and $[M]_y=162·9$, $[M]_g=271·7$.

Malonyl-biscamphorylthiocarbamylhydrazide (II, X=CH_2).—The precipitate obtained on cooling the reaction mixture after 4 hours' heating melted at 162°. The mother liquor yielded on successive dilution two products, m.p. 151° and 183° respectively, the latter on recrystallisation melted at 185°. A further quantity was obtained by redissolving the fractions, m.p. 162° and 151° in little boiling alcohol and rejecting the unreacted camphoryl mustard oil which

crystallised first; the mother liquor contained the required compound. (Found: N, 16·01. $C_{25}H_{38}O_4N_6S_2$ requires N, 15·27 per cent). $[\alpha]_y=29{\cdot}8$, $[\alpha]_g=50{\cdot}7$ and $[M]_y=163{\cdot}9$, $[M]_g=278{\cdot}9$].

Succinyl-biscamphorylthiocarbamylhydrazide [II, $X=(CH_2)_2$].—The product was obtained by precipitating the reaction mixture with water, m.p. 170°. On recrystallisation from dilute alcohol it was obtained in silvery plates, m.p. 176°. [Found: N, 14·7. $C_{26}H_{40}O_4N_6S_2$ requires N, 14·89 per cent). $[\alpha]_y=39{\cdot}7$, $[\alpha]_g=50{\cdot}5$ and $[M]_y=224{\cdot}0$, $[M]_g=284{\cdot}8$].

Glutaryl-biscamphorylthiocarbamylhydrazide [II, $X=(CH_2)_3$] was obtained from the mother liquor of the reaction mixture by dilution with water, the crude product melting at 195-98°. The pure compound was obtained by once crystallising from dilute alcohol in light silvery plates, m.p. 201°. (Found: N, 14·66. $C_{27}H_{42}O_4N_6S_2$ requires N, 14·53 per cent). $[\alpha]_y=12{\cdot}4$, $[\alpha]_g=18{\cdot}6$, $[M]_y=71{\cdot}7°$, $[M]_g=107{\cdot}5$.

Adipyl-biscamphorylthiocarbamylhydrazide [II, $X=(CH_2)_4$] being moderately soluble in alcohol remains in the mother liquor of the reaction mixture and is obtained by precipitating with water. The crude product, m.p. 200-203°, on recrystallisation from dilute alcohol, gave the pure compound as silvery white plates, m.p. 207°. (Found: N, 14·3. $C_{28}H_{44}O_4N_6S_2$ requires N, 14·2 per cent). $[\alpha]_y=33{\cdot}4$, $[\alpha]_g=42{\cdot}4$, and $[M]_y=197{\cdot}7$, $[M]_g=251{\cdot}0$.

Action of terephthalyl *and* isophthalylhydrazides *with camphoryl*isothiocyanate.—The reaction products melted at 169° and 206° respectively. As they were almost insoluble in alcohol and other solvents, their rotatory power could not be determined.

Section C.

p-*Acetaminobenzylidenecamphorquinone-α-hydrazone* (I).—An intimate mixture of *p*-acetaminobenzaldehyde (16 g.) and camphorquinone-α-hydrazone (18 g.) moistened with a little amyl alcohol was heated at 180° in an oil-bath for 3 hours. The reaction product crystallised from alcohol in shining golden yellow needles, m p. 232°, yield 25 g. The substance is insoluble in water, more soluble in hot alcohol and sparingly soluble in benzene and chloroform. (Found: C, 70·27; H, 7·48; N, 12·85. $C_{19}H_{23}O_2N_3$ requires C, 70·15; H, 7·07; N, 12·92 per cent). The substance (0·2504 g.) dissolved in absolute

alcohol (100 c.c.) gave a rotation of 0·12° in a 5 cm. tube. Hence $[\alpha]_D = 95·85°$ and $[M]_D = 311·6°$.

(*i*) The *oxime* crystallised from alcohol in yellow rectangular plates, m.p. 183°. The substance (0·1501 g.), dissolved in 95 % alcohol (100 c.c.), gave a rotation of 0·41° in a 5 cm. tube. Hence $[\alpha]_D = 546·3$ and $[M]_D = 1858·0$. (*ii*) The *semicarbazone* crystallised in fine silky needles from alcohol, m.p. 195°. The substance (0·0976g.) dissolved in 95 % alcohol (100 c.c.) gave a rotation of 0·05° in a 5 cm. tube. Hence $[\alpha]_D = 102·4$ and $[M]_D = 391·4$. (*iii*) The *phenylhydrazone* crystallised from dilute alcohol as pink leaflets, m.p. 205°. The substance (0·1193 g.) in 95 % alcohol (100 c.c.) gave a rotation of 0·09° in a 5 cm. tube, hence $[\alpha]_D = 150·9$ and $[M]_D = 626·2$.

Hydrolysis of the hydrazone by potassium hydroxide solution gave *p*-acetaminobenzaldehyde (*oxime*, m.p. 207°) and camphor.

Hydrolysis with dilute hydrochloric acid or dilute sulphuric acid gave shining plates, m.p. 219° identified to be azocamphanone.

tere*Phthalyldi*-p-*acetphenylenediamine* (II).—To a solution of monoacetphenylenediamine in a little glacial acetic acid, theoretical quantity of *tere*phthalyl chloride was added gradually when the solution became warm and a small quantity of a precipitate separated. On heating the mixture for 1 hour at 120° a pasty mass was obtained which was neutralised with sodium carbonate and on being boiled repeatedly with water, gave an amorphous ash-coloured powder insoluble in all the organic solvents, m.p. 350°. (Found: C, 64·9; H, 6·0; N, 12·9. $C_{24}H_{22}O_4N_4$ requires C, 65·35; H, 5·12; N, 13·0 per cent).

tere*Phthalyl-di*-p-*nitroaniline* (III).—A mixture of *tere*phthalyl chloride (1 mol.) and *p*-nitroaniline (4 mol.) was heated on a water-bath for an hour in presence of benzene. The heavy precipitate was filtered and freed from nitroaniline hydrochloride by washing with water. The residue on boiling with alcohol left a yellow amorphous powder insoluble in all the organic solvents, m.p. 295°. (Found: N, 14·0. $C_{20}H_{14}O_6N_4$ requires N, 13·8 per cent). Isolation of the pure diamine by reducing this compound has not been successful.

tere*Phthalyldiaminoazobenzene* (IV).—A mixture of *tere*phthalyl chloride (7·5 g.), *p*-aminoazobenzene (29·0 g.) and benzene (500 c.c.) was heated for 1 hour. An amorphous orange yellow powder was obtained by repeatedly washing the product with water and alcohol. It does not melt even at 325°. (Found: N, 15·99. $C_{32}H_{24}O_2N_6$.

requires N, 16·08 per cent). This compound could not be reduced by tin and hydrochloric acid to the desired diamine.

Action of 2:7-diaminophenanthraquinol on camphorquinone.—2:7-Dinitrophenanthraquinone was prepared according to the method of Schmidt and Kampf (*Ber.*, 1903, **36**, 3739) which was found to be preferable to the methods of Werner (*Annalen*, 1902, **321**, 336) and Graebe (*ibid.*, 1873, **167**, 143). It was reduced to 2:7-diaminophenanthraquinol by the method of Kleemann and Wense (*Ber.*, 1885, **18**, 2169). The following modifications in the method, however, were adopted with advantage: Tin and hydrochloric acid were used instead of stannous chloride and hydrochloric acid as it hastened the reaction and the solution of the tin double salt was concentrated before removing the tin by hydrogen sulphide thus avoiding the oxidation of the amine during concentration. The amine did not condense with camphorquinone.

4:4′-Dinitrodinaphthylurea (V).—1:4-Nitronaphthylamine was prepared by nitration of α-acetnaphthalide (Lellmann and Remy, *Ber.*, 1886, **19**, 797) and the separation of the 4-nitro compound effected according to Morgan and Micklethwait (*J. Chem. Soc.*, 1905, **87**, 928). 1:4-Nitronaphthylamine (14 g.) was intimately mixed with an equal weight of phenylcarbonate and heated in an oil-bath for an hour at 190° and at 210° for one hour more. The unreacted phenyl carbonate and the phenol formed during the reaction were removed by washing with CCl_4, the insoluble yellow amorphous powder was purified by repeatedly boiling with alcohol, m.p. 275°. (Found: C, 62·7; H, 4·1; N, 14·03. $C_{21}H_{14}O_5N_4$ requires C, 62·7; H, 3·7; N, 13·93 per cent).

4:4′-Diaminodinaphthylurea (VI).—Dinitrodinaphthylurea (10 g.) was heated under reflux with strong hydrochloric acid (100 c.c.) and granulated tin (63·0 g.) for 6 hours, when almost all the tin went into solution and in place of the yellow dinitro compound a flocculent white precipitate remained suspended in the liquid. After cooling the white precipitate was separated by filtration and purified by crystallisation from a large volume of water as shining plates. It left inorganic residue on incineration and was the stannous chloride double salt of diaminodinaphthylurea hydrochloride. (Found: N, 6·9. $C_{21}H_{18}ON_3$, 2HCl, $2SnCl_2$ requires N, 7·0 per cent).

The tin double salt was freed from tin by passing hydrogen sulphide repeatedly in a solution of boiling dilute hydrochloric acid, and the tin-free solution evaporated to dryness in a vacuum when a white

crystalline hydrochloride was left. This, however, on exposure to air rapidly turned pinkish, m.p. above 300°. (Found: N, 11·7.* $C_{21}H_{18}ON_3$, 2HCl requires N, 13·5 per cent).

Dicarbamidodinaphthylurea (VII).—To an aqueous solution of the hydrochloride of (VI, 3 g.) was added an aqueous solution of potassium cyanate (1·5 g.) under ice-cooling, and the separated dicarbamido compound crystallised from water, m.p. above 300°. (Found: N, 20·16. $C_{23}H_{20}O_3N_6$ requires N, 19·63 per cent).

Action of diaminodinaphthylurea with camphorquinone.—A mixture of the hydrochloride of diaminodinaphthylurea (2 g.), sodium acetate (1·6 g.) and camphorquinone (1·6 g.) was heated under reflux in an alcoholic suspension for 8 hours when a dark viscous tarry mass separated. Though the desired camphorquinone condensation product (Calc. N, 8·7 per cent.) could not be isolated a yellow crystalline compouud, m.p. 185°, was obtained from the tarry reaction product by repeatedly precipitating it with petrol from benzene solution and then crystallising from a large volume of petrol (Found: N, 6·3 per cent. $[\alpha]_D = +0·48°$)

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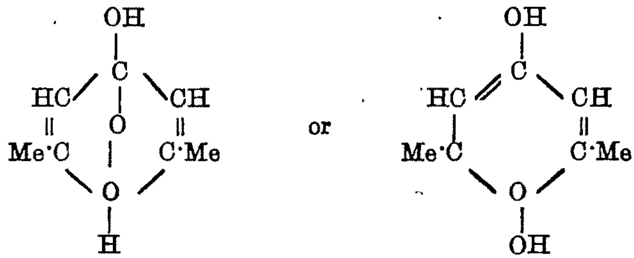
* The low value of nitrogen is evidently due to the presence of some stannous chloride double salt which could not be completely removed though H_2S was passed for more than one dozen times.

Synthesis and Structure of Dipropionylacetone and of Di-*n*-butyrylacetone.

By S. S. Deshapande, Y. V. Dingankar and D. N. Kopil.

Collie's structure of diacetylacetone (I) as against the open-chain ketonic or enolic structure, is based upon facts such as: —



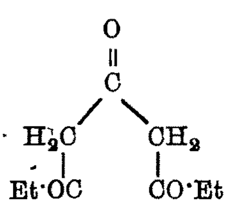
(I)

(*a*) Absence of ketonic reactions in the compound. (Collie, *J. Chem. Soc.*, 1904, **85**, 971).

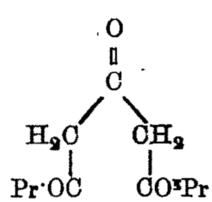
(*b*) Inequivalence of the two replaceable hydrogen atoms in it. (Collie and Reilly, *J. Chem. Soc.*, 1921, **119**, 1550).

This structure is also supported by the value of its molecular refraction determined by Homfray (*J. Chem. Soc.*, 1905, **87**, 1451), which does not agree with the open-chain structure.

To throw more light on the structure of diacetylacetone it was thought desirable to synthesise and study the higher homologues namely dipropionylacetone and di-*n*-butyrylacetone from diethylpyrone and di-*n*-propylpyrone respectively, synthesised by one of us (*J. Indian Chem. Soc.*, 1932, **9**, 303). These compounds to which the structures (II) and (III) respectively may provisionally be given were obtained from the corresponding pyrones as in the preparation of diacetyl-acetone.



(II)



(III)

The compound (II), when freshly distilled, is a yellow liquid which slowly changes into red one, this change being accompanied by change in refractive index and structure. The change is much slower than in the case of diacetylacetone. The yellow and red forms may be called the α- and β- form respectively. The β- form changes back into the α- form on distillation. The two forms give different sets of reactions.

The compound (III) is a brownish yellow liquid and when pure does not seem to undergo a change in its refractive index.

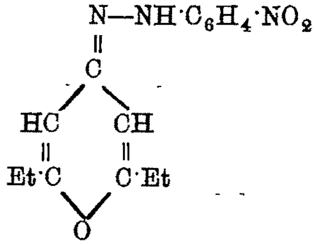
By the action of phenylhydrazine on dimethylpyrone carboxylic acid Feist and Bellart (*Ber.*, 1895, **28**, 1817) obtained a yellow solid having the composition $C_{19}H_{22}ON_4$ and a white solid $C_{19}H_{20}N_4$. They considered the yellow solid to be the diphenylhydrazone of diacetylacetone. This was later prepared by Collie from diacetylacetone itself (*J. Chem. Soc.*, 1922, **121**, 1984) but was found to have the composition $C_{19}H_{20}N_4$ which cannot be that of a diphenylhydrazone. Collie did not investigate the structure of this compound.

Dipropionylacetone and di-*n*-butyrylacetone were treated with phenylhydrazine, but the reaction products were viscous liquids from which no definite compounds could be isolated.

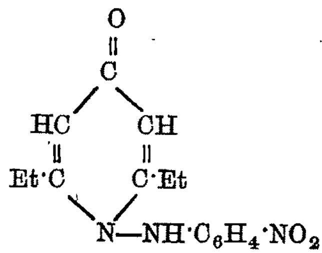
The use of *p*-nitrophenylhydrazine in place of phenylhydrazine gave unexpected results. One molecule of the α-form of dipropionylacetone reacts with 1 molecule of nitrophenylhydrazine with elimination of 2 molecules of water and formation of a compound $C_{15}H_{17}N_3O_3$ melting at 78°. The β- form fails to produce this compound. One molecule of it, however, reacts with 2 molecules of nitrophenylhydrazine and gives with elimination of 3 molecules of water a compound, $C_{21}H_{22}O_4N_6$ melting at 164°.

By the action of the barium salt of dipropionylacetone (1 mol.) and nitrophenylhydrazine hydrochloride (2 mols.) a third compound was obtained (m.p. 141°) having the composition $C_{21}H_{24}O_5N_6$ which is that of a dinitrophenylhydrazone.

None of the compounds melting at 78° and 164° can be a true phenylhydrazone as in their formation the number of water molecules eliminated exceeds the number of nitrophenylhydrazine molecules reacted by one. This additional molecule of water must obviously come from the ketone, a process which will result in ring-formation. (IV) or (V) are, therefore, the possible structures of the compound melting at 78°.

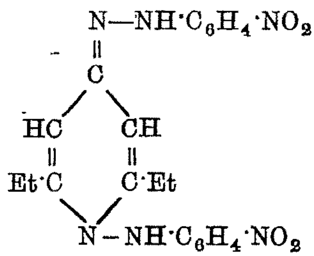


(IV)



(V)

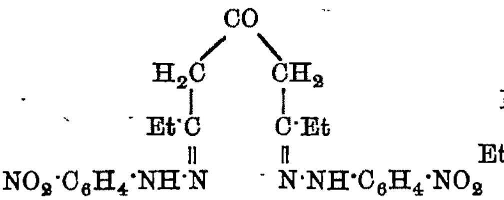
(IV) is nitrophenylhydrazone of diethylpyrone, a compound which has not so far been obtained from diethylpyrone itself (*J. Indian Chem. Soc.*, 1932, 9, 303). (V) is *N*-nitrophenyliminodiethylpyridone. The possible structure of the compound melting at 164° is (VI) which is that of the nitrophenylhydrazone of (V).



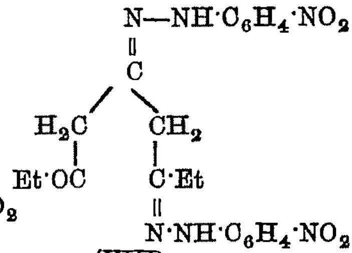
(VI)

The structures are finally confirmed as follows. The compound melting at 164° behaves like a pyridone. It is a mono-acid base and forms a hydrochloride and a chloroplatinate. It also behaves like a phenylhydrazone. On hydrolysis it gives the compound melting at 78°. Both these reactions are in agreement with the structure (VI). As regards the compound melting at 78° the following facts prove that its structure is (V) and not (IV). It is a mono-acid base and forms a chloroplatinate. It is obtained by hydrolysis of (VI) containing two $>N{-}NH{-}C_6H_4{\cdot}NO_2$ groups of which one forming part of the ring cannot be removed during hydrolysis. It is not further hydrolysable to diethylpyrone. The compound (VI) could not, however, be synthesised from (V) and nitrophenylhydrazine.

The dinitrophenylhydrazone melting at 148° is not basic. Its structure can be either (VII) or (VIII).



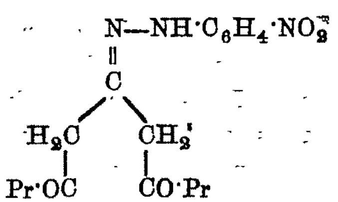
(VII)



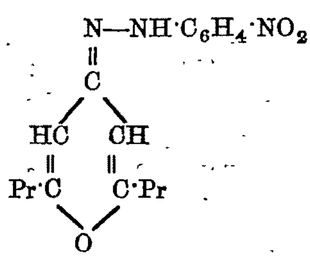
(VIII)

In di-*n*-butyrylacetone the middle carbonyl group yields to phenylhydrazone formation (*vide infra*). If, therefore, one can go by analogy, for the compound melting at 148° the structure (VIII) is preferred to (VII).

Freshly prepared di-*n*-butyrylacetone reacts with one molecule of nitrophenylhydrazine and gives a yellow compound melting at 71° and having the composition $C_{17}H_{23}O_4N_3$ which is that of a mono-nitrophenylhydrazone. The presence of di-*n*-butyrylacetone among the products of hydrolysis of the compound melting at 71° could be demonstrated, which proves that the compound is a true phenylhydrazone. In contact with strong hydrochloric acid and platinic chloride this compound gives a chloroplatinate whose composition is that of the chloroplatinate of nitrophenylhydrazone of di-*n*-propylpyrone (X). It is, therefore, obvious that in the compound melting at 71° the middle carbonyl group of the triketone has yielded to phenylhydrazone formation and, therefore, its structure is (IX).

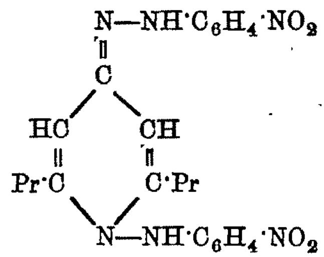


(IX)



(X)

The action of two molecules of nitrophenylhydrazine on di-*n*-butyrylacetone gives the corresponding pyridone phenylhydrazone (XI) which resembles its lower homologue in all its chemical reactions.



(XI)

These reactions of these two triketones can be readily explained by their open-chain ketonic or enolic formulæ.

Experimental.

Dipropionylacetone (II).—To the aqueous solution of pure diethylpyrone was added a hot concentrated solution of barium hydroxide in excess and the mixture heated to boiling for 5 minutes, when the barium salt of dipropionylacetone precipitated as a pale yellow solid. This was filtered, washed and decomposed by cold dilute hydrochloric acid. The ketone separated as an oil which was extracted with chloroform. On drying and removal of the solvent the residual liquid was distilled at 117°/6 mm. (Found: C, 63·7; H, 8·0. $C_9H_{14}O_3$ requires C, 63·5 ; H, 8·2 per cent).

Freshly distilled dipropionylacetone (α-form) is a yellow liquid with a strong pleasant odour. $D_4^{20} = 1{\cdot}032$; $n_D^{20} = 1{\cdot}4999$.

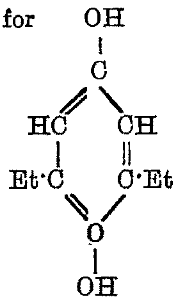
The molecular refraction $\dfrac{n^2-1}{n^2+2}\cdot\dfrac{M}{\alpha} = 48{\cdot}4$

The value calculated for Et·CO·CH_2·CO·CH_2·CO·Et$=44{\cdot}04$

Et·C(OH)=CH·CO·CH=C(OH)·Et $=45{\cdot}92$

Et·C(OH)=CH·C(OH)=CH·C(OH)=CH·Me$=48{\cdot}92$

The value calculated for



$= 47{\cdot}99$ * (using 2·65 as the value of atomic refraction of quadrivalent oxygen indirectly obtained by Homfray, *loc. cit.*).

After standing for 8 days the colour of the compound changed to red and refractive index rose to 1·5044 which then remained constant. The ketone gives violet colour with ferric chloride and forms a sparingly soluble copper salt. When its solution in aqueous methyl alcohol containing a trace of hydrochloric acid is boiled for one hour it is converted into diethylpyrone.

The pyridone (V).—The best yield of this compound was obtained when the ketone (1 mol.) and nitrophenylhydrazine (0·8 mol.) were heated together in absolute alcoholic solution on a water-bath for 20 minutes. On concentrating and leaving overnight the mass became semi-solid which was spread on a porous tile. The solid obtained was crystallised from dilute acetic acid in almost colourless needles m. p. 78°. (Found: C, 62·4 ; H, 5·6 ; N, 15·1. $C_{15}H_{17}O_3N_3$ requires C, 62·7 ; H, 5·9 ; N, 14·7 per cent).

The chloroplatinate of the pyridone was prepared by adding platinic chloride to the solution of the pyridone in strong hydrochloric acid. It is an orange solid melting at 198° [Found: Pt, 20·5. $(C_{15}H_{17}O_3N_3)_2H_2PtCl_6$ requires Pt, 19·8 per cent].

The phenylhydrazone (VI).—The ketone (β-form, 1 mol.) and nitrophenylhydrazine (2 mols.) were heated in absolute alcoholic solution for 20 minutes. On removing the solvent the sticky mass was rubbed with glacial acetic acid, when a yellow solid separated. This was crystallised from pyridine in needles, m. p. 164°. (Found: C, 59·1 ; H, 5·0 ; N, 19·8. $C_{21}H_{22}O_4N_6$ requires C, 59·7 ; H, 5·2 ; N, 19·9 per cent).

* The value 47·99 is given for molecular refraction of dipropionylacetone using a simple ring-formula.

The chloroplatinate of (VI) was prepared as that of (V). It is a yellow solid melting at 157°. [Found: Pt, 15·5. $(C_{21}H_{22}O_4N_6)_2 \cdot H_2PtCl_6$ requires Pt, 15·5 per cent].

Hydrolysis of (VI).—The compound was dissolved in glacial acetic acid and was refluxed for 1 hour in a current of dry hydrochloric acid. On cooling the product was poured into water and the turbid mass filtered. The filtrate deposited on standing a small amount of crystalline compound in the form of needles. This on drying melted at 78° and was identified as the pyridone (V) by mixed melting point.

The dinitrophenylhydrazone (VIII).—Barium salt of the ketone (1 mol.) and nitrophenylhydrazine hydrochloride (2 mols) were well shaken in absolute ether for one day. The ethereal layer was decanted off and the remaining solid was washed repeatedly with dilute acetic acid to dissolve barium chloride and the unchanged substances. The dinitrophenylhydrazone is a brownish yellow solid and was crystallised twice from pyridine in small needles melting at 148°. (Found: N, 19·68. $C_{21}H_{24}O_5N_8$ requires N, 19·1 per cent). The substance was insufficient for estimations of C and H.

Di-n-butyrylacetone (III) was prepared in the same way as its lower homologue. Its barium salt is less readily formed and in smaller yield. The salt is decomposed by exposure to air. The ketone is a liquid showing great tendency to pass into dipropylpyrone, for when it was distilled under reduced pressure the distillate contained the pyrone which was identified in the form of its chloroplatinate. When, however, a small amount of the liquid was quickly distilled it boiled at 136°/ 4 mm. It is a brownish yellow liquid with a strong pleasant odour resembling that of its lower homologue, $n_D^{20} = 1·4856$. It colours ferric chloride violet. (Found: C, 65·9 ; H, 8·6. $C_{11}H_{18}O_3$ requires C, 66·7 ; H, 9·1 per cent).

The copper salt was obtained by shaking the ketone with aqueous copper acetate. It is a bluish green solid insoluble in water and alcohol. (Found: Cu, 24·0. $C_{11}H_6O_3Cu$ requires Cu,24·6 per cent).

The phenylhydrazone (IX).—For the preparation of this compound fresh and fairly pure form of the ketone was required which was obtained from the above copper salt by decomposing it with an acid. When the ketone and nitrophenylhydrazine in equimolecular proportions were heated together in absolute alcohol for 20 minutes and the solvent evaporated the phenylhydrazone was obtained from the residue on rubbing. It was crystallised from alcohol or petroleum ether in

pale yellow needles melting at 71°. (Found: C, 61·4; H, 6·8; N, 13·1. $C_{17}H_{23}O_4N_3$ requires C, 61·3; H, 6·9; N, 12·6 per cent).

When the compound (IX) was left in contact with strong hydrochloric acid and platinic chloride overnight, the *chloroplatinate* of (X) was slowly formed. [Found: Pt, 18·8. $(C_{17}H_{21}O_3N_3)_2H_2PtCl_6$ requires Pt, 18·8 per cent].

The phenylhydrazone (IX) was hydrolysed by dry hydrochloric acid in boiling acetic acid solution. On pouring the solution into water a mass of the unchanged phenylhydrazone precipitated and was removed by filtration. On neutralising the filtrate and boiling with barium hydroxide a small quantity of the barium salt of the ketone (III) separated as a solid. When the barium salt was acidified the ketone was formed and was recognised by its odour and its ferric chloride reaction.

The phenylhydrazone (XI).—It was prepared from the ketone which had stood for some days. Its preparation is similar to that of the compound (VI). It was crystallised from alcohol in deep yellow needles melting at 140°. (Found: C, 61·3; H, 5·2; N, 18·7. $C_{23}H_{26}O_4N_6$ requires C, 61·3; H, 5·7; N, 18·7 per cent).

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The Physico-chemical Characteristics of the Oxides of Nickel from the Magneto-chemical Standpoint.

By S. S. Bhatnagar and Gurbachan Singh Bal.

Recent literature abounds in references to investigations on the methods of preparation and properties of the various oxides of nickel which are important from the standpoint of theory and their application as catalysers in important technical processes.

Leehand and Lepierre (*Bull. Soc. chim.*, 1892, *iii*, 7, 600) were the earliest to report that the two oxides prepared by the ignition of anhydrous nickel sulphate were crystalline modifications of the parent salt and their densities were slightly different from each other. Later Le Blanc and Saeghe (*Z. Elektrochem.*, 1926, **32**, 58) by heating the basic carbonate of nickel to various temperatures ranging from 550° to 1220° obtained nickelous oxide of colours varying from dark grey to greyish green. They, however, showed that most of the oxides possessed the normal cubic structure as evidenced by the patterns of the X-ray diffraction and from this they concluded that there was only one type of NiO formed. The black colour of the oxide was explained on the fact that the oxide adsorbed oxygen from the air forming an adsorption complex.

Prasad and Tendulkar (*J. Chem. Soc.*, 1931, 1403) studied the influence of temperature of preparation on the physical properties of nickelous oxide. They found that with rise in temperature of preparation, the density and the electrical resistance of NiO increased and the rate of dissolution in sulphuric acid and the catalytic actvity in the decomposition of hydrogen peroxide decreased. They concluded that there were two distinct forms of nickelous oxide, the black oxide prepared at 400° and the greenish yellow oxide obtained at 1000°. They ascribed these changes in properties to changes (*i*) in particle size, (*ii*) in crystalline form, and (*iii*) in intramolecular structure.

Recently, Cairns and Ott (*J Amer. Chem. Soc.*, 1933, **55**, 527) from an X-ray study of nickelous oxide have shown that the two

modifications described are identical and have the usual face-centered type of lattice and are not different from each other in an intramolecular way.

On the other hand, a number of higher oxides of nickel have been reported. Rose (*Pogg. Ann.*, 1851, **84**, 671), Glaser (*Z. anorg. Chem.*, 1903, **36**, 1), Baubigny (*Compt. rend.*, 1878, **87**, 1082; 1905, **141**, 1232), Wohler and Blaz (*Z. Elektrochem.*, 1921, **27**, 406), Vaubel (*Chem. Z.*, 1922, **46**, 978) and Lunde (*Z. anorg. Chem.*, 1927, **162**, 352) have reported the preparation of oxides such as Ni_3O_4, Ni_2O_3 and NiO_2.

More recently, Goralevich (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1165) has reported the existence of a number of higher oxides of nickel, *e. g.*, Ni_2O_3, Ni_3O_4 and NiO_2. Besides these, he has also found evidence for the existence of the following composite and less stable oxides:—Ni_5O_9, Ni_6O_{11}, Ni_3O_5, Ni_6O_{17}, Ni_7O_{12}, Ni_8O_{15}, Ni_5O_8, $Ni_{11}O_{17}$, Ni_9O_{16}, Ni_8O_{13}, Ni_5O_7, Ni_2O_3.

The later work of Hendricks, Jefferson and Schultz (*Z. Kryst.*, 1930, **73**, 376) has thrown doubt on the accuracy of Goralevich's work

In view of the above conflicting evidence as to the nature of the black nickelous oxide and the the existence or otherwise of the higher oxides of nickel, it was considered desirable to investigate this problem from the magneto-chemical standpoint.

Experimental.

In general the experiments carried out in this investigation were the following:—

1. Preparation of the nickel oxides by various methods.
2. Estimation of nickel, and the determination of the chemical composition of the oxides.
3. Experimental determination of the magnetic susceptibility χ of the various samples.
4. Experimental determination of the temperature coefficient of χ for the two samples of NiO.
5. Adsorption of oxygen by the two oxides.

The following methods were employed to prepare the oxides under investigation:—

(*a*) By heating nickel nitrate (extra pure) very strongly on the blow-pipe flame.

(*b*) By melting nickel chloride with potassium chlorate.

(c) By treating nickel salts in solution with potassium hypochlorite acq.

(d) By heating the hydroxide (i) on the blow-pipe flame, and (ii) on the Bunsen burner flame.

(e) By heating nickel carbonate in air.

(f) Treating the nickel chloride solution with hydrogen peroxide in cold and afterwards adding the alcoholic potash solution.

The amount of nickel in these oxides was estimated by the dimethylglyoxime gravimetric method.

Some of the results were checked by the potassium cyanide volumetric method and as this involved the use of potassium cyanide for most of the work, the gravimetric method alone was employed.

From the analytical investigations of the reaction products obtained in the various methods the following results were obtained.

TABLE I

Method of preparation.	Wt. of the product.	Oxide expected to be formed.	Wt. of nickel Obs.	Calc.
1. Heating the nitrate on the blow-pipe flame	0·0699 g. (dark green)	NiO	0·0547 g.	0·0551 g.
2. Heating the carbonate on the blow-pipe flame	0·0706 (black)	NiO	0·0581	0·0556
3. Heating the mixture of nickel nitrate and potassium chlorate on the blow-pipe flame, till fusion	0·0773 (black)	Ni_2O_3	0·0547	0·0549
4. Heating the hydroxide on the blow-pipe flame	0·0790	NiO	0·0614	0·0622
5. By adding sodium hypochlorite to nickel nitrate solution	0·0734 Some hydrate formation took place and the weight of Ni was found to be less than that of oxygen	Ni_2O_3	0·0341	0·0521
6. Treating the nickel chloride solution with hydrogen peroxide in cold and afterwards adding the alcoholic potash solution	0·0469 A green mass was first obtained which turned black on drying	NiO_2	0·0351	0·0369

As pure NiO was expected to be formed from methods, 2 and 4, the reaction products resulting from these methods were analysed for Ni only. The weight of oxygen was determined by difference.

In the case of methods No. 1 and No. 3, observed amounts of nickel compared well with the calculated amounts. From this coincidence it may appear as if the reaction products were pure oxides. But these results are not convincing, unless the above conclusions are confirmed by the determination of the oxygen content and physical properties of these substances, such as densities and magnetic susceptibilities.

Density determinations of all the oxides were carried out by suspending them in toluene and employing the usual specific gravity bottle method.

A Gouy's type balance was used for the magnetic measurements. It consisted of a very sensitive Sartorious balance placed on a hollow wooden box. One of the two pans of the balance was replaced by a half pan similar to the type used in Sp. G. determinations of lighter bodies. To this half pan was soldered a hollow copper cylinder about three inches in length and two inches in diameter through which a copper rod R having a hook at the end was passed and this rod could be moved upwards and downwards inside the hollow cylinder by means of a screw, which provided the arrangement for raising or lowering the sample tube inside the magnetic field. The balance resembled the equipment shown in Baird and Tatlock's catalogue.

Determination of χ.—After setting the balance in order, its standardisation was undertaken. Copper sulphate (A. R.) of known susceptibility was put in the sample tube up to a definite mark and the pull exerted on the sample tube in the magnetic field was measured. By using the relation $mg=\frac{1}{2}AH^2(K_1-K_2)$ the value, of AH^2 was determined (K_1 and K_2 in this equation represent the volume susceptibilities of the material of the cylinder and the medium). A current of 1·5 amps. was passed through the solenoids and the value of AH^2 was found to be 0·7162.

In order to test the accuracy of this value of AH^2 the susceptibilities of the following known substances were measured and were found to compare well with the well known values of χ for these substances.

TABLE II

Name of the substance.	Observed value of $\chi \times 10^6$.	Actual value of $\chi \times 10^6$.
Cobalt sulphate (crystals) extra pure	36·95	37·0
Nickel sulphate, extra pure	15·80	16·0
Iron ammonium sulphate, extra pure	31·50	32·0

Magnetic susceptibility and density determination by the above methods gave the following results.

TABLE III:

Oxide obtained by.	Wt. of the product.	Wt. of the pull.	Vol. susceptibility $+\chi \times 10^6$.	Mass susceptibility $+\chi \times 10^6$.	Density.
1. Heating the nitrate very strongly on the blow-pipe flame	0·9613 g.	0·0186 g.	271·783	53·4	5·2
2. Heating the carbonate on the blow-pipe flame	0·6756	0·0020	45·504	8·12	5 6
3. Heating the mixture of nickel nitrate and potassium chlorate to fusion	0·9608	0·0038	56·467	10·88	4·8
4. Heating the hydroxide on the blow-pipe flame	0·9034	0·0033	47·869	9·97	5·19
5. Adding sodium hypochlorite to nickel nitrate soln.	0·4196	0·0036	52·627	23·49	2·24
6. Treating the nickel chloride solution with hydrogen peroxide in cold and afterwards adding alchoholic potash solution	0·9126	0·0035	46·856	9·52	4·8

In all the above pull measurements the tube was filled to the same volume and the current passed in all the cases was also the same.

The value of χ for the oxide prepared by the first method was found to be $53{\cdot}4 \times 10^{-6}$. This compared very favourably with the value $53{\cdot}7 \times 10^{-6}$ obtained by Honda (*Sci. Rep. Tohoku Imp. Univ.*, 1914, **3**, 113; 1915, **4**, 215) for pure nickel oxide.

It will be shown later that this value of χ was not a proof of the composition of NiO and that the coincidence with the value obtained by Honda was purely accidental as the correct value of χ for NiO has been found to be $9{\cdot}56 \times 10^{-6}$. The high value ($53{\cdot}4 \times 10^{-6}$ is due to the partial reduction of the oxide to the metallic nickel owing to the introduction of a small quantity of carbon from the blow-pipe flame.

In the first stage of ignition a black sample (the value of χ being $9\cdot12 \times 10^{-6}$) was obtained which on further heating for 6 to 8 hours gave value of χ even higher than $53\cdot4 \times 10^{-6}$ and it was noticed that the tube began to stick to the poles of the electromagnet. The appearance of ferromagnetism introduced a new complication and the investigation was then pursued as follows:

The ferromagnetic variety obtained above when heated in an electric furnace to a temperature of 1000° lost its property of ferromagnetism, the value of χ was found to be $53\cdot4 \times 10^{-6}$, which is identical with our first value. On further heating the sample it was found that the value of susceptibility showed a further decrease. A plausible explanation of this might be that a compound of the type Ni_3O_4 has been formed at some particular temperature. As Ni_3O_4 is analogous to Fe_3O_4 (a highly magnetic substance) and as Fe_3O_4 decomposes to FeO, similarly the compound Ni_3O_4 (ferromagnetic) should undergo decomposition to NiO (paramagnetic). If it is so then the above views regarding the magnetic properties of the compound, on heating, could be qualitatively accounted for. In order to provisionally fix the temperature of production of the ferromagnetic sample, a series of experiments were made which gave the following results.

TABLE IV.

Process.	Colour.	$\chi \times 10^6$.
1. Heating the black oxide on the blow-pipe flame	Dark green	Ferromagnetic
2. Heating the black variety in the electric furnace	Dark to green	Black 9·11 Green 9·56
3. Heating the black oxide in a sealed crucible	Dark green after 6 to 8 hours	Ferromagnetic
4. Heating the black oxide in a silica tube	The colour becomes green on continuous heating	9·56 to 10·01
5. Heating the ferromagnetic variety in an electric furnace	Colour changes from dark green to distinct green	The value of χ falls to 9·56

From Table IV it is quite obvious that the samples obtained on blow-pipe flame yield very high values of χ, while the products electrically obtained are feebly paramagnetic. This difference in the magnetic nature of the products could be accounted for in various ways such as the following:

(1). Formation of Ni_3O_4 and its subsequent change to NiO. This view had to be discarded altogether because of the non-formation of the ferromagnetic sample in the electric furnace at any temperature whatsoever. And the values of χ never exceeded the figure $9{\cdot}56 \times 10^{-6}$ in any case. If at a particular temperature, Ni_3O_4 had been formed, the results would have been identical both when the sample was heated either electrically or on a Bunsen flame.

(2). The magnetic field of the electric furnace might be responsible for the production of a different type of NiO. But this again would not explain the magnetic behaviour of the products obtained in the silica tubes which were similar to the products of the electric furnace. It could thus be safely inferred that the presence or absence of the magnetic field was without any effect on the magnetic nature of the products obtained in the two cases.

(3). While the products of reaction or decomposition were being heated on the blow-pipe flame, it is possible that a small amount of carbon or unburnt gas might have found entrance into the reaction mixture and this might have resulted in the formation of traces of free metallic nickel, by the reduction of the oxide, which being highly ferromagnetic might have rendered the sample ferromagnetic on the whole. This possibility is altogether ruled out when the product is obtained in an electric furnace.

(4). The gaseous products evolved during the decomposition might have changed the nature of the product formed.

The following experiments were, therefore, carried out to settle these points.

I. A small amount of carbon was added to the black oxide and the mixture again heated in the electric furnace more strongly. This resulted in the production of a very strongly ferromagnetic sample.

II. (*a*) The black oxide was heated in sealed crucibles on the blow-pipe flame. The resulting products were ferromagnetic in character.

(*b*) When silica tubes were used instead of the crucibles, the samples produced gave values of χ identical with those obtained in the electric furnace. This proves the entrance of carbon and gases through porous crucibles as opposed to the silica tubes.

III. When a ferromagnetic variety was brought in contact with a magnet it was found that a very small part of the sample was

attracted to the magnet and this on analysis was found to be metallic nickel.

IV. In order to study the influence of temperature on the nature of the resulting products, the ferromagnetic variety was heated in an oxy-acetylene and oxy-coal gas flame, respectively. In both cases the value of χ fell very low. Paramagnetic black oxide when heated under similar conditions and cooled showed no change in the values of χ.

The results of these experiments, when taken together, lead definitely to the view that the ferromagnetic sample is the result of the reduction of nickel oxide to nickel. This view finds support from the following work on the temperature coefficient of χ of the ferromagnetic variety.

Temperature Coefficient.

In order to determine the variation of χ with T a very small electric furnace was devised as follows:—

Two rectangular mica plates were taken, round which a very fine 'eureka' wire was wound in opposite directions so that the current flowing in one may cancel the magnetic effect of the current flowing in the other. The number of turns on both the plates was also identical. These wires were covered from outside by two similar mica plates held together with small supports of fine copper wire. The temperature could thus be very easily regulated by adjusting the strength of the current flowing though the circuit.

This small furnace with two sets of mica plates, the distance of which could be changed, was introduced in the gap, each plate being a little apart from the pole piece. The sample tube was introduced in the usual manner in the gap and so inside the two mica plates. The weight of the sample tube along with the oxide was determined every time (at every temperature) before putting the field on. Afterwards the tube was weighed in the field, the difference between the two weighings gave us the pull. In this way the effect of the current flowing in the furnace, if any, could be eliminated. Now as the mica plates got heated they also raised the temperature of the adjoining poles which changed the value of AH^2. To avoid this, an attempt was made to keep the two magnets at almost the the same temperature throughout the experiment by a special cooling arrangement.

Cooling arrangement.—The magnets were covered by two double walled vessels of almost the same shape as the pole pieces in which cold water was circulated. This kept the magnets at a uniform temperature though the temperature of the gap was very near to 400°.

While studying the variations of χ with T in the case of ferromagnetic variety the following results were obtained.

TABLE V.

$AH^2 = 1{\cdot}9272$. Wt. of the sample$=0{\cdot}2567$ g.

Current passed in the furnace.	Temp.	Pull.	$\chi \times 10^6$.
0·0 amp.	29·4°	0·0082 g.	32·48
0·1	73·8	0·0081	32·07
0·2	129·0	0·00805	31·87
0·28	146·5	0·0080	31·66
0·35	231·8	0·0079	31·26
0·38	292·8	0·0078	30·85
0·40	355·4	0·0077	30·44
0·41	362·0	0·0077	30 44
0·42	366·0	0·0032	12·63

From Table V it is evident that at 365° the ferromagnetic variety loses its ferromagnetism altogether and becomes moderately paramagnetic yielding the valuable information that metallic nickel is the cause of the ferromagnetism of the so-called nickel oxide as the temperature 365° coincides with the 'Curie point' of nickel.

A study of the temperature variation of χ of green and black variety of the oxides was undertaken and the results obtained are given in the following table.

TABLE VI.

$AH^2=1{\cdot}9272$. Wt. of the green oxide$=0{\cdot}2041$ g. Wt. of the black oxide $=0{\cdot}1284$ g.

	Green oxide			Black oxide		
Current passed in the furnace.	Temp.	Pull.	$\chi\times10^6$.	Temp.	Pull.	$\chi\times10^6$.
0·00 amp.	28·6°	0·0019 g.	9·48	25·0°	0·00115 g.	9·11
0·15	66·2	0·00185	9·22	57·2	0·0011	8·71
0·25	114·6	0·00175	8·72	129·6	0·0010	7·93
0·28	141·4	0·0017	8·45	204·2	0·0009	7·13
0·30	191·2	0·0016	7·94	242·8	0·00085	6·72
0·35	248·6	0·0015	7·43	319·2	0·00075	5·94
0·38	292·6	0·0014	6·90	351·4	0·0007	5·60
0·40	351·6	0·0013	6·318			

Although the original values of χ for the two samples are different the curves for χ and T in both the cases run parallel and the changes in values of χ per unit temperature within this range are identical. These results will be discussed later.

Adsorption of Oxygen by the Two Nickelous Oxides.

Investigations on this point were necessary as the black oxide of nickel on desorption of oxygen becomes green. The reverse phenomenon does not appear to have been investigated at all.

The apparatus used for the purpose was Lunge's gas volumnometer, and it was modified to suit our purpose as follows:

A glass tube of about 1″ in diameter at the top drawn at the bottomto a fine bore of about 1/10″ in diameter, and about 2 ft. in length was connected by means of a special mercury-rubber tubing to a 50 c.c. burette having a three-way cock at the top. By means of this three-way cock, the burette could be connected with the sample tube or with the calcium chloride cylinders which were introduced for drying the gas passing through them.

In the first instance the burette was filled with air by means of a pulley arrangement which helped in raising or lowering the mercury in the burette.

Fresh and dry air was introduced by the said device and the connection with the sample tube was made and both the time and level of the mercury in the burette was noted.

After 24 hours the oxygen was collected in an aspirator from which it was introduced in the burette. The observations in the case of black oxide yielded negative results while the green variety clearly manifested an adsorption, though small. The values of χ were found to be:

$\chi \times 10^6$ before adsorption $= 9 \cdot 38$

$\chi \times 10^6$ of green sample after a slight adsorption of $O_2 = 9 \cdot 26$

$\chi \times 10^6$ of black sample $= 9 \cdot 11$

This clearly indicates that the value of χ tends to change towards the direction of the black variety when oxygen is adsorbed by the green sample. The next two sets of experiments were performed to get further information on this point.

(*a*) Freshly prepared oxygen was passed over the green oxide which had already absorbed oxygen both at room temperature and at 260° for over 8 hours. It was found that no further change in the value of χ occurred at all beyond that recorded above.

(*b*) To investigate the matter still further a little of the oxide was placed on a perforated plate sufficiently above the mixture of potassium chlorate and manganese dioxide so that the freshly evolved oxygen may get a chance to come in contact with a large surface of the green oxide.

Even in this case no change was observed and the green oxide retained its green colour and did not assume the black colour. While the black oxide easily becomes green on losing adsorbed oxygen when heated, the reverse experiment seems to be possible only when the green oxide comes into contact with active oxygen and evidently the value of $9 \cdot 11 \times 10^{-6}$ for χ is indicative of the limit of the adsorbability of active oxygen by this oxide.

The Case of the Oxide of the Composition Ni_2O_3.

During the preparation of nickel oxides by various methods, a sample, black in colour, which on analysis found to be Ni_2O_3, was obtained (*cf.* Table I, No. 5). Its density and susceptibility were also determined the values being 4·8 and $10 \cdot 88 \times 10^{-6}$ respectively.

As in the case of NiO previously described, important differences in magnetic properties were noticed when the sample was prepared in the electric furnace. It was, therefore, considered desirable to check these results in an analogous manner.

By changing the method of preparation of the oxide (by using electric furnace instead of Bunsen burner or blow-pipe flame for heating), the final product obtained was similar in all chemical and physical characteristics to NiO. The values for density and χ were 6·6 and $9{\cdot}58 \times 10^{-6}$ respectively. The analytical results for oxygen and nickel also denoted a composition NiO.

The experiment was repeated several times and the results indicated that Ni_2O_3 could not be formed by method No. 8 (Table I).

From this it is concluded that the production of Ni_2O_3 by No. 8 method on the blow-pipe flame must have been accidental owing to the introduction of certain impurities from the flame.

The presence of nickel in these cases was also established by the 'Curie point' method, as well as from actual analysis of oxygen and nickel ratio.

Summary and Discussion of Results.

1. Various methods used in the preparation of nickel oxides result in reaction products, many of which on analysis are found to be chemically identical, though they possess distinct colours.

2. Two prominent colours, black and green, are generally exhibited by different oxide samples. In certain cases compounds of intermediate type composed of varying quantities of the two oxides, possessing colour dark green to faint black, are also obtained.

3. While the difference in colour is attributed to the difference in various physical conditions of the samples, *viz.*, (*a*) particle size, (*b*) crystalline form, (*c*) intramolecular nature (Prasad and Tendulkar, *loc. cit.*), it has been shown that traces of adsorbed gases, particularly of oxygen, and the presence of other impurities in minute quantities can bring about a marked change in the colour and magnetic properties of the reaction products.

4. That the presence of traces of impurity which gets introduced in the sample while it is being heated, cooled and purified, or while

it is being carried to some other similar operation, can change both the physical and chemical nature of the substance to a very great extent, is fully borne out by the fact that the sample obtained on the blow-pipe flame contains free nickel and carbon and gives highly ferromagnetic product due to the presence of free nickel.

5. That in these oxides, the presence of free nickel is analytically difficult to estimate, is due to the fact that the presence of carbon renders the estimations inaccurate, the amount of nickel found by estimations being always lower than the actual amount. The value of χ ($63{\cdot}4 \times 10^{-6}$) for nickel oxide points to the fact that Honda's compound was made on the blow-pipe flame and contained traces of free nickel as impurity.

The preparation of nickelous oxide in an electric furnace gives a substance which on analysis is found to be chemically pure NiO and the value of χ for this never exceeds $9{\cdot}56 \times 10^{-6}$.

6. That the higher value of χ reported before is due to the presence of varying qualities of nickel. This view has been confirmed by many other experiments, the most important of them being the determination of the susceptibility of the ferromagnetic variety at various temperatures. The sudden change in the value of χ at 365°, which is the same as the 'Curie point' of the metallic nickel, clearly shows that the ferromagnetic variety does contain traces of free nickel which becomes paramagnetic at the 'Curie point'.

The formation of ferromagnetic variety by heating a mixture of carbon and nickel oxide in the furnace, sticking of a part of the ferromagnetic oxide to a magnet which on subsequent analysis is found to be nickel, as well as the results obtained from the silica tube experiments, support the same view.

7. That the value of χ for nickelous oxide prepared in the silica tube in place of a crucible is also $9{\cdot}56 \times 10^{-6}$ adds further support to the above view.

8. The χ and T curves of the two nickelous oxides run parallel showing thereby that both the varieties have got almost the same temperature coefficient for χ. The black oxide retains the lower value of χ throughout the experiments and clearly establishes that while the two nickel oxides are chemically identical the lower value of χ for the black sample is due to some difference in its physical nature such as adsorption of oxygen.

9. The results of adsorption experiments are in accordance with X-ray diffraction photographs obtained by Cairns and Ott (*loc. cit.*).

These two investigators attribute the black colour of the oxide as being due to the adsorption of active oxygen. It has been found that the black oxide on heating very strongly is turned green owing to the liberation of adsorbed oxygen. Adsorption results indicate that the green variety can adsorb more oxygen than the black one which already contains some oxygen. The adsorption of oxygen by the green variety tends to lower its value of susceptibility as shown by the adsorption experiments. If sufficient adsorption of oxygen takes place by the green variety, it is possible that it may become black giving th same value of χ as the black sample.

10. The various oxides reported in literature were most probably formed by the introduction of certain impurities from outside. The only oxide of nickel which can be produced under various experimental conditions is NiO, the existence of which has been proved definitely. This possesses definite physical and chemical characteristics.

11. From the adsorption results obtained in this investigation and which are in line with the *X*-ray work of Cairns and Ott (*loc. cit.*), the view that the intramolecular changes may be brought about seems to be superfluous as all the facts can be accounted for on the impurities, oxygen and nickel getting incorporated with the NiO during experimentation.

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Photolysis of Amino Acids in Sunlight.

By G. Gopala Rao and N. R. Dhar.

From the standpoint of soil fertility the nitrogenous portion of the soil is of paramount importance. Most of the nitrogen added to the soil by ploughing under sod, plant stubble, green and stable manure, is in the form of proteins and their decomposition products. These substances cannot be assimilated by higher plants as such, but have to be broken down to ammonia and then oxidised to nitrate. The nitrates are then assimilated by the plants.

It was at first thought that organic matter can be nitrified directly. But, Muntz (*Compt. rend.*, 1890, **110**, 1206) has shown that organic matter has to be decomposed first and ammonia liberated, before nitrates can be formed. Omeliansky (*Cent. Bakt.*, 1899, **5**, 473; 1902, **9**, 63) also obtained negative results for urea, asparagine, methylamine and egg-albumin; so that he concluded that all forms of organic nitrogen have to be transformed first into ammonia before they can be nitrified and utilised by the plant. The decomposition of organic nitrogenous compounds with the liberation of ammonia is commonly known as ammonification From what has been said above it will be evident that ammonification is an important chemical process occurring in the soil.

The isolation of a number of amino acids from the soils by Schreiner and Shorey (*U.S. Dept. Agr. Bur. Soils Bull.* No. 74) and Lathrop (*J. Amer. Chem. Soc.*, 1912, **34**, 1260) has demonstrated that the process of decay of proteins takes place through the stage of amino acids. The amino acids give rise to ammonia by further processes of hydrolysis and oxidation.

Muntz (*loc. cit.*) was the first to demonstrate that organic nitrogenous matter is decomposed by micro-organisms with the formation of ammonia. Muntz and Coudon (*Compt. rend.*, 1893, **116**,395) have further shown that no ammonia was formed in sterile soil in two

and half years, while the unsterilised soil produced in sixty seven days 41 to 100 mg. of ammonia per 100 g. of soil. These investigations were followed by those of Marchall (*Cent. Bakt.*, 1895, **2**, 753) and numerous others which pointed out the importance of ammonia formation in the soil and the rôle of micro-organisms in its formation from proteins. This was found to be not a specific property of certain bacteria, but a function of a large number of micro-organisms and fungi.

In the light of the above experimental evidence it is believed that ammonification in soils is solely due to the action of bacteria and fungi. It is important to observe that the experiments of all those investigators were conducted in the dark. Now the present authors have studied the decomposition of various nitrogenous compounds like amino acids, amides, amines, proteins, etc., in aqueous solution in the presence of sunlight and photocatalysts like titanium dioxide, aluminium trioxide, humic acid, zinc oxide, etc. These experiments have revealed that most nitrogenous compounds are decomposed into ammonia, which may then be oxidised to nitrite, and nitrate and in a recent communication (*J. Indian Chem. Soc.*, 1933, **10**, 699) it has been shown that light not only plays an important rôle in nitrification but it is of great importance to ammonification, which is mainly an oxidation reaction. In this paper the influence of light on the oxidation of some amino acids has been investigated in the absence of bacteria.

The amino acids are oxidised to ammonia, carbon dioxide and an aldehyde containing one carbon atom less. The change can be represented by the equation,

$$R{\cdot}CH{\cdot}NH_2COOH+(O) \longrightarrow R{\cdot}CHO+NH_3+CO_2.$$

We have also observed that the rate of photo-oxidation of amino acids is greater than that of ammonia to nitrate. Hence there is less likelihood for the simultaneous formation of nitrite in the experiments on photo-ammonification, specially in view of the fact that no air was passed through the exposed solutions continuously. Besides, it has been shown in publications from these laboratories that reducing substances act as negative catalysts in oxidation reactions. The aldehyde formed in the photo-oxidation of amino acid would, therefore, inhibit the further oxidation of ammonia to nitrite. Thus in our experiments we have observed the formation of only traces of nitrite.

EXPERIMENTAL.

The amino acids used in this investigation were obtained from Kahlbaum. The requisite amount of the amino acid was dissolved in sterile water and the solution poured into a sterile Erlenmeyer flask of pyrex glass containing a definite amount of photosensitiser and then plugged with sterile cotton wool. Thereafter the flask was exposed to sunlight. An exactly similar flask was kept in the dark as a blank and every precaution was taken to avoid bacterial contamination in these light and dark experiments. The blank solution did not develop any ammonia, while the one exposed to sunlight showed a steady increase in the amount of ammonia formed. The non-formation of ammonia in the dark (blank) solution shows the freedom from contamination of the experimental solutions with any ammonifying organisms.

Methods of analysis.—The determination of ammonia was done by the improved Folin aeration method, using sodium carbonate to liberate the ammonia. The residual amino-nitrogen was determined by the van Slyke method.

Glycine.—250 C.c. of a solution of $M/20$-aminoacetic acid were exposed to sunlight with and without photosensitiser under strictly aseptic conditions. There is a slow but definite oxidative decomposition in sunlight in glass vessels without any photosensitiser. In quartz vessels the decomposition is more rapid. The photolysis in the presence of photosensitisers, like titanium dioxide, is considerably more rapid; hence this photosensitised oxidation was studied in greater detail. Analysis of the reaction products has shown that the actual decomposition of the amino acid can be represented as

$$CH_2 \cdot NH_2COOH + (O) \rightarrow HCHO + NH_3 + CO_2.$$

The amount of ammonia-nitrogen formed was estimated by the Folin aeration method; and the amount of amino-nitrogen disappeared has been determined by the well known van Slyke method. The following results show that the amount of NH_3-nitrogen corresponds almost quantitatively to the decrease in the NH_2-N. The following table shows the progress of the photolysis of glycine with time in the presence of titanium dioxide,

TABLE I.

250 C.c. of $M/20$-glycine+0·25 g. of TiO_2 exposed in a glass flask to sunlight for 80 hours.

NH_2-N in g./10 c.c. Before.	After irradiation.	Diff. decrease in NH_2-N.	Folin NH_3-N.
0·006980	0·005817	0·001163	0·001160

TABLE II.

250 C.c. of $M/20$-glycine+0·25 g. of TiO_2 exposed to sunlight in a glass flask. Amount of NH_2-N per litre=698 mg.

Time (hr.)	...	40	80	120	160
NH_3-N (mg./litre)	...	28·82	115·28	185·00	244·30
Decomposition (%)	...	4·13	16·50	26·64	35·00

Under the conditions of the experiment only minute traces of nitrite were formed.

Photodecomposition of anthranilic acid.—$M/20$-solution of anthranilic acid (*o*-aminobenzoic acid) was exposed to sunlight in a pyrex glass flask with titanium dioxide, under conditions which excluded bacterial contamination. After a few hours' exposure the solution assumed a deep red-brown colour. Analysis revealed the presence of aniline. It appears, therefore, that preliminary decomposition of anthranilic acid can be represented by the equation,

$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} \longrightarrow C_6H_5NH_2 + CO_2.$$

Prolonged exposure resulted in the formation of ammonia which was estimated by the Folin aeration method. The results are recorded in the following table,

TABLE III.

250 C. c. of $M/20$-amino acids with 0·25 g. of catalyst were exposed to the sun in a glass flask under sterile conditions. 20 C. c. portions were withdrawn from time to time and ammonia liberated was estimated by Folin's method.

Amino acids.	Time of exposure. 40 hrs.		80 hrs.		120 hrs.		160 hrs.		200 hrs.	
	NH_3-N (mg./litre).	decom-position.	NH_3-N (mg./litre).	decom-position.	NH_3-N (mg./litre).	decom-position.	NH_3-N (mg./litre).	decom-position.	NH_3-N (mg./litre).	decom-position.
Glycine + TiO_2	28·82	4·13 %	115·28	16·5%	185·00	26·64%	244·3	35%	...	...
Alanine + TiO_2	43·23	6·2	86·5	12·40	129·80	18·76	...	...	217·54	31·20%
Alanine + ZnO	160·21	23·01	319·82	45·80	478·56	68·66	...	...	...	...
Alanine + Al_2O_3	4·50	0·645	9·21	1·3	13·7	1·96	19·4	2·78	...	...
Aspartic acid + TiO_2	25·22	3·6	50·48	7·23	75·60	10·83	...	...	125·00	17·90
Aspartic acid + ZnO	71·29	10·21	142·10	20·3	213·42	30·57	...	...	...	...
Asparagine + TiO_2	50·44	3·61	115·28	8·26	172·18	12·7	...	...	...	...
Glutamic acid + TiO_2	25·22	3·6	50·44	7·2	75·64	10·84	...	...	124·60	17·82

TABLE IV.

250 C. c. $M/20$-anthranilic acid + 0·25 g. of TiO_2 exposed to sunlight.

Time (hr.)	40	80	120
NH_3-N formed (mg./litre).	14·41	21·61	27·76
Decomposition %	2·06	3·09	4·12

Hippuric acid is very stable in sunlight even in the presence of photosensitisers.

SUMMARY.

1. The photolysis of various amino acids in sunlight has been studied. These amino acids decompose with the liberation of ammonia. The decomposition appears to be one of oxidative de-amination. The aliphatic amino acids, *e.g.*, glycine are oxidised in the presence of air and sunlight with the formation of the corresponding aldehyde, ammonia and carbon dioxide. This is represented by the general equation,

$$R{\cdot}CH{\cdot}NH_2{\cdot}COOH + (O) \rightarrow R{\cdot}CHO + NH_3 + CO_2.$$

2. In most of the cases, the amount of ammoniacal nitrogen formed by photolysis was found to correspond quantitatively to the decrease in amino-nitrogen.

3. From the experimental results it will be seen that monoamino-dicarboxylic acids like aspartic acid and glutamic acid ammonify less readily than the monoaminomonocarboxylic acid like glycine and alanine. It will also be seen that aromatic amino acids like anthranilic acid and hippuric acid, ammonify much less readily than the aliphatic ones.

4. In the light of the above experimental evidence, the authors believe that the formation of ammonia in the soil from amino acids obtained from protein decomposition is mainly an oxidative de-amination, accelerated by sunlight. We have shown that aqueous solutions of amino acids photolyse in the presence of photosensitisers like titanium dioxide, aluminium oxide, humic acid, zinc oxide, etc., when we keep in mind that the first three substances normally occur in all soils it will be clear that ammonification in soils can take place without the presence of bacteria or fungi, if only sunlight be present.

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Photolysis of Amides and Amines in Sunlight

By G. Gopala Rao and K. Madhusudanan Pandalai.

In a previous publication Gopala Rao and Dhar (*vide*, p. 617) have shown that amino acids are oxidised in aqueous solution in the presence of air and sunlight with the liberation of ammonia. The view has been given out that the formation of ammonia from amino acids in the soil is, at least in part, a photochemical process, and can take place without the presence of bacteria and fungi, if only sunlight be present.

In the present paper the experimental results on the photolysis of amides and amines in sunlight have been recorded. Our experiments show that amides are first hydrolysed in aqueous solution with the formation of the corresponding ammonium salt, when exposed to sunlight in the presence of photosensitisers like titanium dioxide. There is no reaction in the dark under the experimental conditions. This is unlike the behaviour of animal charcoal which according to Warburg can catalyse the oxidation of amino acids in the dark by oxygen. Further, if a slightly basic substance like calcium carbonate be present, the ammonia of ammonium salt is oxidised to nitrite.

Experimental.

Photo-oxidation of Amides.

The requisite amount of the amide (Merck) was dissolved in sterile water and the solution poured into a sterilised Erlenmeyer flask of pyrex glass containing a definite amount of the photosensitiser, and the flask was then plugged with cotton wool. It was then exposed to sunlight every day from 10 A. M. to 4 P.M.

A definite volume of the solution was withdrawn by a sterile pipette from time to time; and the amount of ammonia obtained was determined by the Folin æration method ; the nitrite formed was estimated in another sample of the solution by the Griess-Ilosvay colorimetric method or the iodometric method developed by Gopala Rao and Pandalai (*Analyst*, 1934, 59, 99).

Formamide.—$M/20$-formamide solution (100 c.c.) was exposed to sunlight in a sterile glass flask with 1 g. of calcium carbonate and 0·1 g. of titanium dioxide. The results are recorded in Table I.

TABLE I.

Amount of amido-nitrogen per liter=700 mg.

Time of exposure.	NH_3-N.	Nitrite-N.	Total N.	% decomp.
10 hr.	60 mg./litre	Nil	60·30	8·57
20	125	0·09 mg./litre	125·09	17·87
30	192	0·15	192·15	27·45
50	340	0·21	340·21	48·60

Acetamide.—$M/20$-aqueous solution of acetamide (100 c.c.) was exposed to sunlight in a pyrex glass flask with 1 g. of calcium carbonate and 0·1 g. of titanium dioxide. A definite volume of the solution was withdrawn from time to time and the ammonia and nitrite contents determined. The results are tabulated below.

TABLE II.

Amount of amido-nitrogen per litre=700 mg.

Time of exposure.	NH_3-N.	Nitrite-N.	Total N.	% decomp.
10 hr.	25·0 mg./litre	Nil	25·00	3·57
20	45·3	2·50 mg./litre	47·80	6·83
30	68·28	6·30	74·58	10·65
50	123·61	12·49	136·10	19·44

Benzamide.—$M/20$-solution of benzamide (100 c.c.) was exposed to sunlight in a pyrex glass flask with 1·0 g. of calcium carbonate and 0·1g. of titanium dioxide. The solution became yellowish-brown after a few hours' exposure. The NH_3-N was estimated by the Folin method and the nitrite-nitrogen by the colorimetric method.

TABLE III.

Time of exposure.	NH_3-N.	Nitrite-N.	Total N.	% decomp.
20 hr.	15·00 mg./litre	Nil	15·00	2·14
50	36·00	0·217 mg./litre	36·217	5·17
80	60·00	0·820	60·83	8·69

It will be evident from a comparison of results in Tables I, II and III that the rate of formation of ammonia from benzamide is much slower than from acetamide or formamide.

Urea.—$M/20$-aqueous solution of urea (100 c.c.) was exposed to sunlight in a pyrex glass flask with 1g. of calcium carbonate and 0·1g. titanium dioxide. The ammoniacal nitrogen was estimated by the Folin method and the nitrite nitrogen by the colorimetric method. The following results show that urea is ammonified and nitrified quite readily.

TABLE IV.

Amount of amido-nitrogen per litre=1400 mg.

Time of exposure.	NH_3-N.	Nitrite-N.	Total N.	% decomp.
10 hr.	25·00 mg./litre	1·50 mg./litre	26·5	1·89
20	47·80	2·30	50·1	3·58
40	90·32	8·40	98·72	7·05

Oxamide and succinimide.—$M/20$-aqueous solutions of oxamide and succinimide (100 c.c each) were exposed to sunlight for 50 hours with 1·0 g. of calcium carbonate and 0·1 g. of titanium dioxide. The results are as follows.

TABLE V

Substance.	NH_3-N.	Nitrite-N.	Total N.	% decomp.
Succinimide	64 85 mg./litre	1·2 mg./litre	66·068	9·438
Oxamide	50·44	8·17	52·61	7·516

Phthalimide.—$M/20$-aqueous solution (100 c.c.) was exposed to sunlight with 1·0 g. of calcium carbonate and 0·1 g. of the photosensitiser, titanium dioxide. After a few hours' exposure to sunlight the solution assumed an yellow colour. Ammonia was slowly formed and no nitrite could be detected even on exposure for 50 hours.

TABLE VI.

Time of exposure.	NH_3-N.	Nitrite-N per litre.	Total N.	% decomp.
50 hr.	25·22 mg./litre	Nil	25·22	3·6

It will be seen from the results recorded in the foregoing pages that aromatic amides and imides decompose much less readily than the aliphatic ones. Benzamide ammonifies much slower than formamide or acetamide.

Among the aliphatic, the amides of monobasic acids decompose more quickly than those of dibasic acids.

Photo-oxidation of Amines.

Methylamine.—$M/5$-aqueous solution of methylamine (200 c.c.) was exposed to sunlight with 0·4 g. of ZnO for 40 hours. Formaldehyde, methyl alcohol and ammonium nitrite were detected in the reaction mixture. The first stage of the reaction appears to be one of hydrolysis.

$$CH_3 \cdot NH_2 + H_2O \rightarrow CH_3 \cdot OH + NH_3$$

This is followed by oxidation of ammonia to nitrite and of methyl alcohol to formaldehyde.

Ethylamine.—When treated in exactly the same manner ethylamine was found to yield ethyl alcohol, acetaldehyde and ammonium nitrite. As in the former case the first stage of the reaction appears to be a case of hydrolysis, represented by the equation,

$$CH_3CH_2NH_2 + H_2O \rightarrow CH_3 \cdot CH_2OH + NH_3.$$

This was followed by the oxidation of ammonia to nitrite and of ethyl alcohol to acetaldehyde.

Dimethylamine yielded formaldehyde and ammonium nitrite when exposed to sunlight in the presence of zinc oxide.

Aniline.—200 C.c. of distilled water with a quantity of pure aniline calculated to make the mixture $M/5$ concentration were exposed in a glass flask to sunlight for 40 hours with 0·4 g. of ZnO. After a few hours' exposure the solution assumed a deep brown colour, and in course of time deposited a brown resinous mass. The amount of nitrite formed was small.

Dimethylaniline when treated in the above manner turned brown, but no nitrite was formed.

The following table gives the amount of nitrite formed in each case.

TABLE VII.

200 C.c of $M/5$-amine in water + 0·4 g. of ZnO exposed to sunlight for 40 hours.

Substance.	Amount of nitrite-N.
Methylamine	35·83 mg./litre
Ethylamine	22·96
Diethylamine	15·56
Aniline	0·28
Dimethylaniline	Nil

From the foregoing results it will be evident that the aliphatic amines are more readily oxidised to nitrite than the aromatic ones. Among the aliphatic amines, the smaller the number of carbon atoms the greater is the tendency for the decomposition.

Discussion.

In our previous publication we have shown that amino acids are oxidised photochemically in aqueous solution, when exposed to sunlight in the presence of photosensitisers like titanium dioxide with the liberation of ammonia. In the present paper we have shown that amides also undergo photochemical oxidation when exposed to sunlight in the presence of photosensitisers like titanium dioxide or zinc oxide, with the ultimate formation of ammonium nitrite. Thus it appears that diverse nitrogenous compounds decompose in the presence of sunlight and air with the formation of ammonia and nitrite.

In the soil nitrogenous compounds undergo similar changes and it is believed that these changes are brought about by the activities of the micro-organisms of the soils, which are specific in their action. The ammonifying organisms of the soil liberate ammonia from the complex nitrogenous compounds, and the ammonia will then be oxidised by the nitrifying bacteria. Now it is interesting to note that sunlight alone can also accomplish all these changes. Hence, we believe that the process of ammonification and nitrification of nitrogenous compounds in the soil may be mainly photochemical in tropical countries, taking place under the influence of sunlight without the interference of bacteria.

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Chemical Reactivity and Light Absorption. Part III.

By N. R. Dhar and P. K. Kar.

In previous publications of this series (*J. Indian Chem. Soc*, 1934, **11**, 33, 311) it has been shown that the light absorption by a mixture of two reacting substances is greater than the absorptions of the reacting substances considered separately. This reaction is found to be applicable to numerous chemical reactions. It seems that whenever there is a possibility of the occurrence of a chemical change by mixing two or more substances, increased light absorption by the mixture is likely to be observed.

Further work has been carried out on this line with reactions involving iodine and the results are recorded in this paper.

Iodine and Acetone.

It has been shown in Part II (*loc. cit.*) that the light absorption by a mixture of acetone and iodine is greater than the absorptions of acetone and iodine taken separately. We have studied this reaction further in different spectral regions and it will be observed from the following photographs that there is increased light absorption in the ultraviolet and visible regions with the mixture, but so far we have not been able to detect any enhanced absorption in the infra-red region. In this reaction hydrochloric acid is added to accelerate the reaction.

The photograph as shown in Fig. 2 was taken with a light filter in order to isolate some particular spectral regions. One quartz cell contained a saturated solution of cobalt chloride and the other 0·06% of K_2CrO_4 solution. These filters were placed next to the source of light and then the reaction vessel. The light coming out of these was photographed (Fig. 2).

Photographs were also taken with a E_1 type of quartz spectrograph and one of them is submitted here (*cf.* Fig. 1).

Infra-red Absorption.

In order to study the light absorption in the near infra-red, ordinary photographic plates were sensitised.

The following sensitising solution was prepared: water-alcohol mixture (85:60) 150 c.c., neocyanin solution (1:2000 in absolute alcohol) 1·5 c.c., kryptocyanin solution (1:1000 in absolute alcohol) 2 c.c., dicyanin solution (1:100 in absolute alcohol) 2·5 c.c. To this solution was added concentrated ammonia (5·5 c.c.), all these mixings being carried on in the dark. Ilford Empress plates were dipped in the above solution for 5 minutes and then rinsed for ½ minute in alcohol and rapidly dried before a fan.

The plates thus sensitised showed lines up to 9500Å but require long exposure. In our experiments, long exposures could not be given as the products of the reaction might take part in the light absorption. Hence, lines up to 8000Å could only be obtained with these plates after an exposure lasting for 45 seconds. Photographs were taken in an Adam Hilger constant deviation glass spectrophotometer. The lines were standardised from a standard emission spectrum of copper arc in Eder's Atlas.

The photograph as given in Fig. 3 shows the light absorption by sodium nitrite solution and aqueous iodine and their mixtures in the infra-red region. Similar results were obtained with acetone and iodine.

As there are no strong lines in the region of 7000Å with copper arc as the source of light, it is difficult to say whether any absorption takes place in that region. But this can be said with a certain amount of definiteness that no absorption takes place at 8000Å.

It is well known that the absorption spectra of iodine vapour consists of a band system extending from the red to the green. There is also a much weaker band system in the near infra-red with a maximum at 7800Å. Another set of bands occurs in the ultraviolet between 2750 to 1700Å. The photographs as given in Fig. 1-4 show that aqueous iodine has absorption in the region 4500 to 5000Å and again selective absorption in the ultraviolet after 3194Å, but no appreciable absorption has been observed in the near infra-red.

Aqueous iodine and potassium oxalate, sodium nitrite, sodium citrate, sodium tartrate and sodium lactate.—A few photographs with concentrated solutions of the above reducing agents and aqueous iodine were taken with a E_1 Hilger quartz

spectrograph with copper arc as the light source. All the photographs show markedly increased absorption in visible and ultra-violet regions with the mixtures of iodine and the reducing agent in comparison with the two reacting substances considered separately. One of the typical photographs is reproduced in Fig. 4.

Relation between Velocity of Thermal Reaction and Light Absorption.

In Part II of this series, it has been stated that under comparable conditions, those reactions, which are fast show greater light absorption with mixtures than in the case of reactions which are slow.

In order to obtain exactly comparable results, we have determined the light absorptions with mixtures containing $M/5$ solutions of the reducing agents and $N/437$ aqueous iodine and the comparative velocities of the reactions in the dark have also been measured by mixing 25 c.c. of each of the solution of the reducing agent and 25 c.c. of the same aqueous iodine at 25° and titrating with a standard sodium thiosulphate solution. Two of the photographs showing increased light absorption by the mixtures, are reproduced in Figs. 5 and 6.

In Table I the increased light absorption by mixtures of the reducing agents and iodine and the comparative velocities of the reactions in the dark at 25° are recorded.

TABLE I.

	Reactants.	Amount of increased absorption.	$N/2371{\cdot}2$ thio consumed after 6′. (Dark velocity in decreasing order)
1.	Hydrazine sulphate (2 c.c.) + conc. HCl	Almost nil	Extremely rapid
1.	Hypophosphorous acid	23Å	5·7 c.c. (in 3′.)
2.	Sodium formate	73	4·9
4.	Ferrous sulphate	360	2·35
5.	Sodium malonate	73	1·6
6.	Sodium nitrite	1605	1·3
7.	Sodium citrate	248	0·95
8.	Sodium lactate	73	0·9
9.	Sodium malate	377	0·8
10.	Acetone	513	0 6
11.	Sodium tartrate	73	0·6
12.	Phosphorous acid	Almost nil	Nil
13.	Potassium oxalate	513 Å	Nil

The right column shows the amount of sodium thiosulphate consumed in 6 minutes in decreasing order, *i.e.*, the order of the dark velocity of the reaction between the reducing agents and iodine. The central column gives the amount of increased light absorption with mixturers of reducing agents and iodine under identical condition.

From the above table we find that the dark velocity of the reaction between potassium oxalate and iodine is practically nil in 6 minutes, but the amount of increased light absorption is 513Å, and the dark velocity of the reaction between sodium formate and iodine is fairly high but the increased light absorption is only 73Å. Similarly the velocity of reaction between hypophosphorous acid and iodine is great but the absorption is as low as 23Å.

Hence, it can be stated that no quantitative relation exists between the dark velocity of reaction and the amount of increased absorption.

Relation between the Heat of Reaction and Amount of Increased Light Absorption.

In order to study how the binding forces of the molecules of iodine are weakened by the presence of reducing agents, the heat of the reaction between the reducing agents and iodine solution was determined.

Experimental procedure.—The heat of the reaction was estimated calorimetrically, a highly polished silver calorimeter being used. The calorimeter was placed in an air-jacket, and the whole apparatus was enclosed in a wooden box and the experimental room was closed on all sides in order to avoid a draft and thus ensuring against external temperature variations. A Beckmann thermometer was used to note the temperature. The reacting solutions were placed in a thermostat so that the temperatures of both the solutions were constant. The calorimeter was tested by putting in 50 c.c. of water in it and noting the temperature at intervals. It was found that the temperature remained constant for 5 hours. 25 C.c. of the reactants were put in the calorimeter and the temperature of the mixture noted after stirring well. The rise in temperature of the mixture was noted at regular intervals until the temperature of the mixture was constant. Each experiment was repeated and the mean of the two results is recorded. 25 C.c. of each solution were mixed in all cases. The results are recorded in Table II.

TABLE II.

Heat of reaction between reducing agents and iodine solutions.

Composition of the mixtures.	Initial temp.	Final temp.	Period to attain final temp.	Heat of reaction per g. atom of I_2.
M-$NaNO_2 + N/826{\cdot}4$-I_2	1·29°	2·70°	$7\frac{1}{2}$ hr.	1,078,856 Cal.
$M/5$-$FeSO_4 + N/61{\cdot}85$-I_2	2·84°	4·64°	$5\frac{3}{4}$	257,904
$M/5$-Na-formate $+ N/65{\cdot}8$-I_2	1·1°	1·61°	$4\frac{1}{2}$	78,702
$M/H_3PO_2 + N/62{\cdot}8$-I_2	1·45°	1·595°	$\frac{3}{4}$	21,226·4

TABLE III

Reducing agents.	Amount of increased absorption with mol. conc. of reactants.	Heat of reaction.
Hypophosphorous acid	23 Å	21,226·4 Cal.
Sodium formate	73	78,702·0
Ferrous sulphate	860	257,904·0
Sodium nitrite	1605	1,078,856·0

The order of increased light absorption is $NaNO_2 > FeSO_4 > H{\cdot}CO_2Na > H_3PO_2$; and the heat of reaction follows the same order. Moreover, it has been calculated from thermochemical data by Dhar and Bhattacharya that the heats of the reactions of potassium oxalate and halogens are as follows: $K_2C_2O_4 + Cl_2$, 84 Cal; $K_2C_2O_4 + Br_2$, 62 Cal; $K_2C_2O_4 + I_2$, 32 Cal; and their light absorptions also follow the same order, *viz.*, the absorption due to $K_2C_2O_4 + Cl_2$ is the maximum, then comes $K_2C_2O_4 + Br_2$ and lastly $K_2C_2O_4 + I_2$.

It appears, therefore, that the greater the heat of a reaction, the greater is the chance of the loosening of the binding forces of the molecules and consequent increased light absorption.

SUMMARY.

1. Increased light absorption for mixtures have been observed in the ultraviolet, and visible regions but not in the infra-red region, with several reactions involving aqueous iodine.

5. The increased light absorption is due to activation of molecules which is associated with the weakening of the binding forces of the molecules.

3. No quantitative relation exists between the velocity of a reaction in the dark and increased light absorption.

4. It appears that the heat of the reaction and increased light absorption by mixtures go hand in hand.

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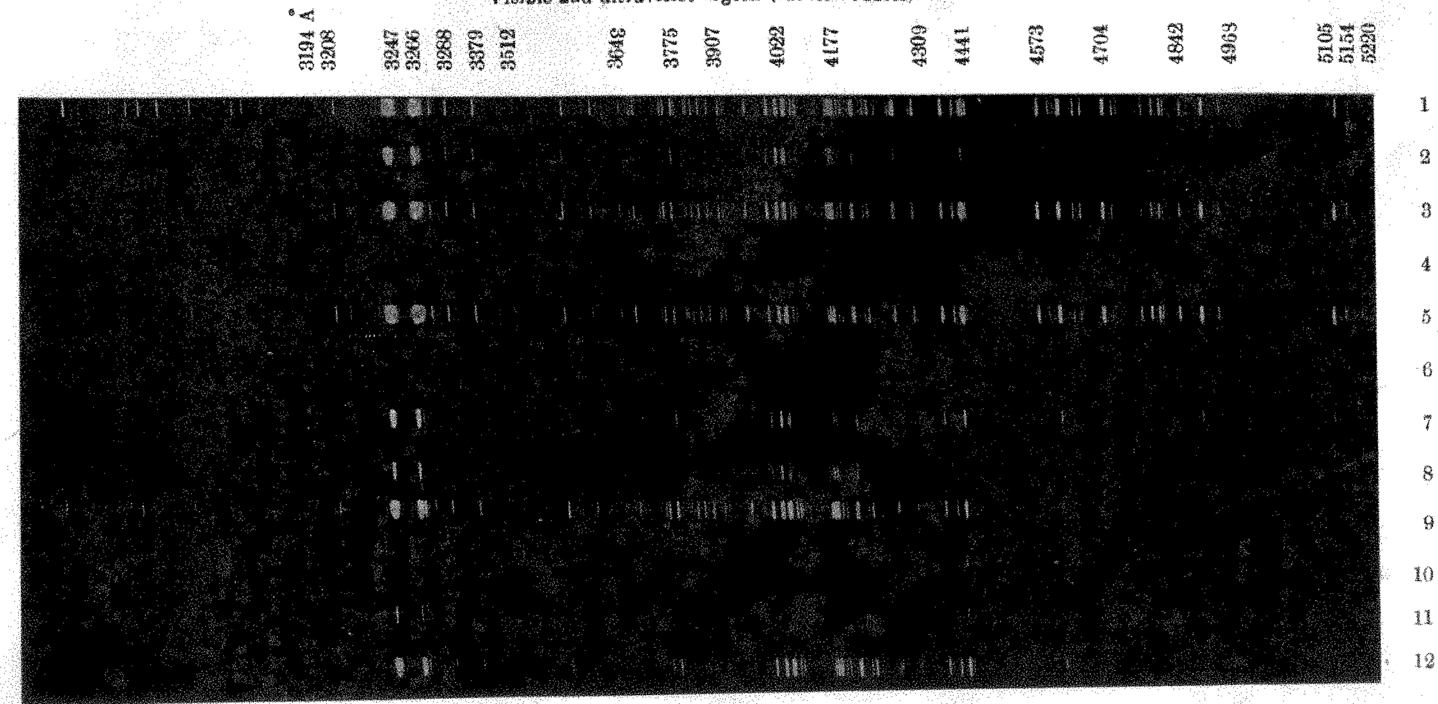
FIG. 1.

Visible and ultraviolet region (3194Å—5220Å).



Exposure—30 sec.

1. Copper arc. 2. 20 c.c. $N/700$-I_2. 3. 20 c.c. 2% acetone. 4. $N/350$-I_2 + 4% acetone. 5. 20 c.c. 1·25% acetone. 6. 2·5% acetone + $N/350$-I_2. 7. 20 c.c. 0·5% acetone. 8 1% acetone + $N/350$-I_2. 9. 20 c.c. $N/1400$-I_2 10. $N/700$-I_2 + 4% acetone. 11. 20 c.c. $N/1400$-I_2 + 2·5% acetone. 12. $N/700$-I_2 + 2·5% acetone.

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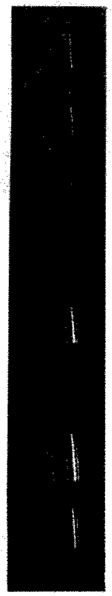
FIG. 2.



Exposure—30 sec.

Range of transmission (3290—2961Å) ; mean 3125Å.

1. Copper arc
2. 20 c.c. 2% acetone (3100Å)
3. 20 c.c. $N/700-I_2$ (3100Å)
4. 4% acetone + $N/350-I_2$ (total absorption)
5. 20 c.c. 1·25% acetone (2961Å)
6. 2·5% acetone + $N/350-I_2$ (3274Å)
7. 0·25% acetone (2961Å)
8. 0·5% acetone + $N/350$ I_2 (3150Å)

FIG. 3.

5218Å 5700Å 6125Å 8000Å

1
2
3
4

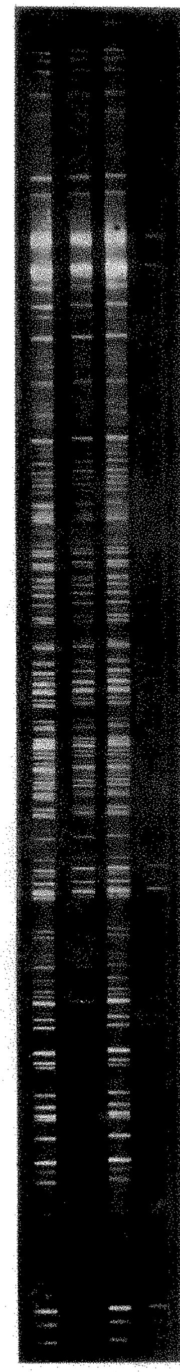
Exposure—30 sec.

1. Cu–arc.
2. 20 c.c. $N/700$-aq. I_2
3. 20 c.c. $N/2-NaNO_2$
4. 20 c.c. $N-NaNO_2+N/350$-aq. I_2.

FIG. 4.

1 2 3 4

3247Å
3266

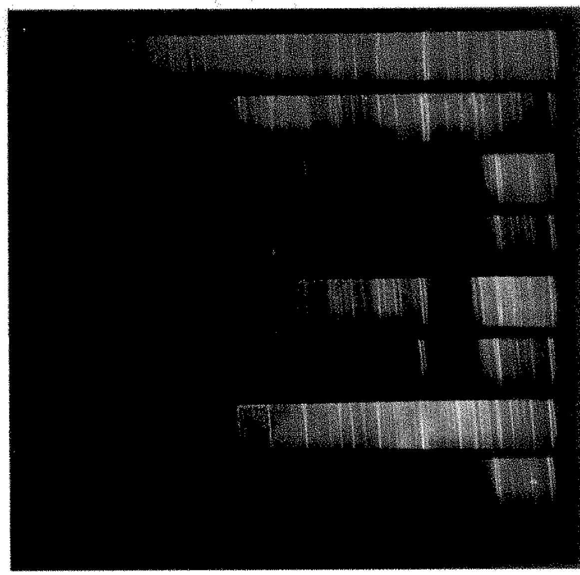


5105
5220

1) Cu-arc. 2) 20 c.c. $N/800$-aq. I_2 (selective absorption). 3) 20 c.c. N-$K_2C_2O_4$ (slight selective absorption). 4) $N/400$-aq.I_2 + $2N-K_2C_2O_4$ 4022Å and selective absorption in visible region).

FIG. 5.

$N/5$-$NaNO_2$ + $N/437$ – aq. I_2 (exposure—10 sec.).



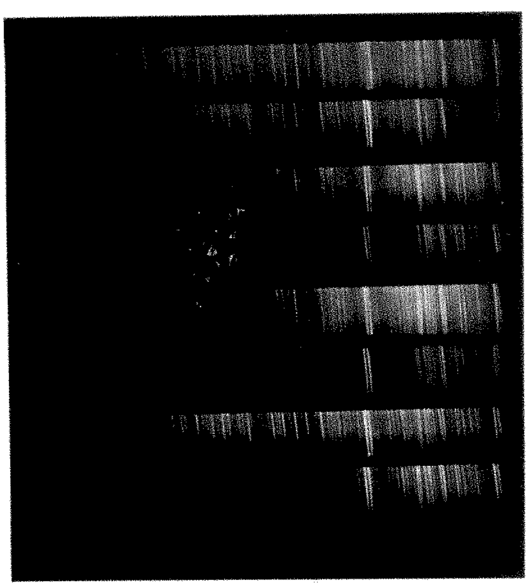
1
2
3
4
5
6
7
8

1. Cu-arc. 2. 20 c.c. $N/874$ – aq. I_2(2370Å). 3. 20 c.c. $M/10$ – $NaNO_2$(2576Å). 4. $N/437$ – aq. I_2 + $M/5$ – $NaNO_2$(3975Å). 5. 20 c.c. $M/20$ – $NaNO_2$. 6. $M/10$ – $NaNO_2$ + $N/437$ aq. I_2. 7. 20 c.c. $N/1748$ – aq. I_2. 8. $N/874$ – aq. I_2 + $M/5$ – $NaNO_2$.

Increase in absorption (3975 – 2370)Å = 1605Å

FIG. 6.

$M/5$ – $FeSO_4$ + aq. I_2 – $N/437$ (exposure—10 sec.).



1 Cu – arc

2 20 c.c. $N/894$ – aq I_2 (2370Å)

3 20 c.c. – $M/10$ – $FeSO_4$ (2618Å)

4 $N/437$ – aq. I_2 + $M/5$-$FeSO_4$ (3230Å)

5 20 c.c. $M/20$ – $FeSO_4$

6 $M/10$ – $FeSO_4$ + $N/437$ – aq. I_2

7 20 c.c. $N/1748$-aq. I_2

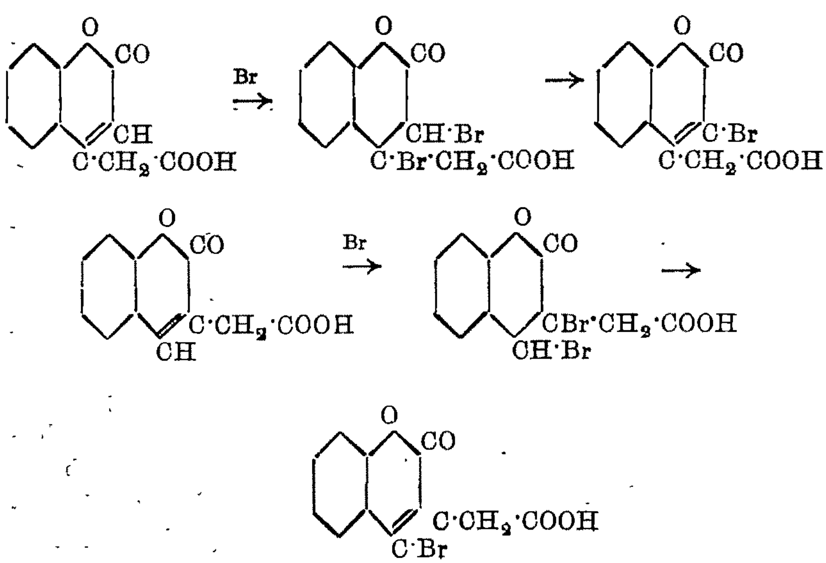
8 $M/5$ – $FeSO_4$ + $N/874$-aq. I_2

Increase in absorption (3230 – 2370)Å = 860Å

Action of Chlorine and Bromine on Coumarin-4- and Coumarin-3-acetic Acids: Coumarin-3- and -4-halogenoacetic Acids and 4-Halogenomethylcoumarins.

By B. B. Dey and (Miss) K. Radhabai.

Coumarin-3 and 4-acetic acids comprise within their molecules a double bond between carbon atoms 3 and 4 in the pyrone ring and a reactive methylene group attached to either of these atoms. A study of the action of chlorine and bromine on these acids was, therefore, expected to yield results of considerable interest by revealing the relative affinities for halogen of the methylene group and the ethenoid linkage. If the usual rule of the halogen attacking primarily the double bond in the pyrone ring were followed in this case without the interference of any possible influence exerted by the reactive methylene groups, an unstable dihalide readily changing, in the case of the coumarin-4-acetic acids into the 3-halogeno acid and in the case of the coumarin-3-acetic acids into the 4-halogeno acids should result thus:—



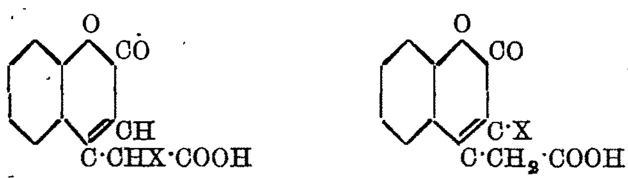
It is to be noted, however, that if the induced polarities of carbon atoms 3 and 4 in the crotonoid system $-\overset{+}{C}H=\overset{-}{C}H-\overset{+}{C}=\overset{-}{O}$, contained in coumarins be taken into account, they would be expected to influence materially these reactions and diminish greatly the probability of bromine being added to the double bond, particularly in coumarin-3-acetic acids.

Preliminary experiments showed that there was very little action at laboratory temperatures and exposure to direct sunlight did not effect any improvement. The best results were obtained by heating in glacial acetic acid at the temperature of the boiling water bath though in the case of the coumarin-4-acetic acids, a considerable amount of decarboxylation ensued and the product, a mixture of the halogenated acid and the decarboxylated body, had to be separated finally by cold sodium carbonate. It was observed as a general rule that decarboxylation occurred to a smaller extent with the chloro than with the bromo acids, the neutral compound being the main product obtained in the latter case under the conditions of experiment. β-Naphthapyrone-4-acetic acid provided the only exceptional case in which neither chlorination nor bromination caused any appreciable decarboxylation, but the product in this case is differently constituted. The halogenation of the coumarin-3-acetic acids was found to proceed much more slowly, a period of 5-6 hours' heating at 100° being normally required for completing the reaction. There was, however, no decarboxylation in this case and the product dissolved completely in cold sodium carbonate. This is to be explained by the superior stability of the 3-acetic acids which unlike the 4-acetic acids, do not decompose even at their melting points (*cf.* Dey and Sankaranarayanan, *loc. cit.*).

The halogenated acids, as is to be expected, proved to be stronger acids than the parent compounds ; while the latter were easily liberated from a solution of their sodium salts by dilute acetic acids, the halogenated bodies did not separate from the alkaline solutions until they were treated with mineral acids. This difference has been utilised in working out an excellent method of separating a mixture of the two acids. The halogenocoumarin-4-acetic acids decomposed at their melting points quantitatively into CO_2 and halogeno-4-methylcoumarins which were found in every case to be identical with the product, insoluble in sodium carbonate, obtained during halogenation. These were neutral compounds, very sparingly soluble in boil-

ing alcohol and having an irritant action on the skin. Nascent hydrogen (zinc-copper couple) reduced them to the 4-methylcoumarins; the replacement of halogen by hydrogen occurring smoothly and quantitatively.

The position of the halogen in the products is deduced from the following considerations: That the halogen could not have entered the benzene ring is proved by (*a*) their behaviour with boiling aqueous alkali which completely removes the halogen, and (*b*) oxidation, halogen-free salicylic and hydroxynaphthoic acids or their homologues being formed. Their remains little doubt, therefore, that the halogen has either entered the pyrone ring or substituted one of the methylene hydrogen atoms, the following alternative structures for the halogenated coumarin-4-acetic acids thus becoming possible:—



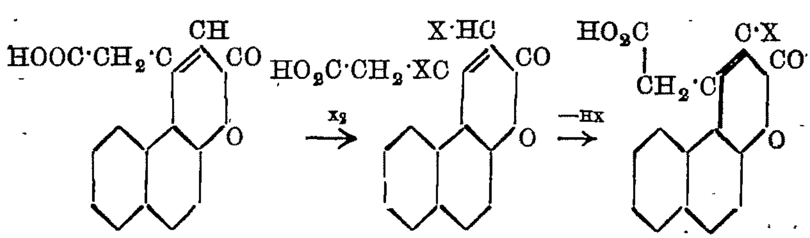
(I) (II)

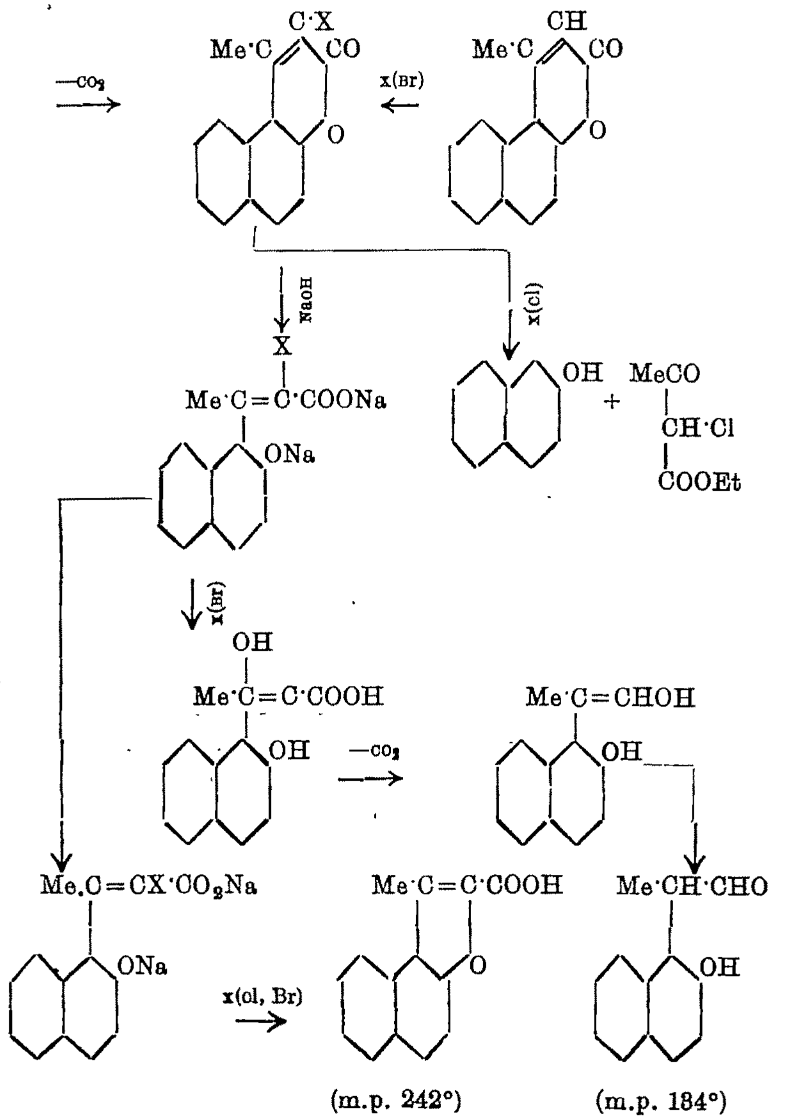
It has been easy to decide between these two constitutions by studying the products obtained by (*a*) decomposition at their melting points and (*b*) heating with alkalis. The compounds formed by loss of CO_2 were found to be quite different from the 3-halogeno-4-methylcoumarins which have been prepared directly from 4-methylcoumarins by treatment with halogens (Simonis and Wenzel, *Ber.*, 1900, **33**, 1961; Fries and Lindemann, *Annalen*, 1914, **404**, 65; Dey and Dalal, *J. Chem. Soc.*, 1923, **123**, 3386) and also in a few cases by condensation of a phenol with α-chloroacetoacetic ester (Dey, *J. Chem. Soc.*, 1915, **107**, 1606). Thus, while 3-bromo-4-methylcoumarin (Simonis and Peters, *Ber.*, 1908, **41**, 832) melted at 115°, the bromo-4-methylcoumarin obtained by decarboxylation of the bromocoumarin-4-acetic acid was found to melt at 176°, similarly 3-bromo-4-methyl-α-naphthapyrone (Dey, *loc. cit.*) melted at 232°, while the corresponding product of decarboxylation of the α-naphthapyrone-4-acetic acid derivative melted at 197°, the melting points being considerably lowered in both cases by admixture.

A clearer proof of the view that the halogen atoms were not attached to position 3 in the pyrone ring is derived from a study of

the action of alkalis on these compounds. The products were well crystallised unsaturated acids isomeric with, but quite different from the benzfuran-2-carboxylic acids which have been prepared from the 3-halogenated coumarins. Structure (I) must therefore be accepted for these acids.

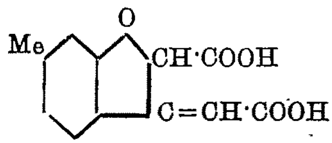
$\beta\alpha$-1:2-Naphthapyrone-4-acetic acid forms, however, a solitary exception to this general rule. A careful examination of the product obtained by decarboxylating the halogenated acid showed that it was not the hydrogen atom of the reactive methylene group but that attached to the carbon atom 3 which had been replaced by halogen. The bromo-β-naphthapyrone-4-acetic acid decomposed on melting into a bromo-4-methylcoumarin which crystallised from alcohol in needles (m. p. 146°), not depressed by admixture with an authentic specimen of 3-bromo-4-methyl-$\beta\alpha$-1:2-naphthapyrone (Bacovescu, *Ber.*, 1910, 43, 1280). Similarly, the product of chlorination of β-naphthapyrone-4-acetic acid yielded on decomposition a product (m.p. 137°), which was identified as 3-chloro-4-methyl-$\beta\alpha$-1:2-naphthapyrone by preparing a specimen of the latter by the condensation of β-naphthol with ethyl α-chloroacetoacetate in presence of sulphuric acid and determining the mixed melting point. Moreover, the results of alkali treatment of these bodies are in complete accord with the theory that they are 3-halogenocoumarins. Thus, the chloro derivative gave a mixture of 3-chloromethyl-β-naphthacoumarinic acid (m.p. 149°) (Dey, *loc. cit.*) and 3-methyl-β-naphthafuran-2-carboxylic acid (m.p. 240°) (Dey and Lakshminarayanan, *private communication*), while the bromo derivative yielded the same furancarboxylic acid (m.p. 242°) together with a product melting at 134° which has been shown (Dey and Lakshminarayanan, *private communication*) to be 2-hydroxynaphthyl-α-propionic aldehyde. The evidence is summarised in the following scheme.



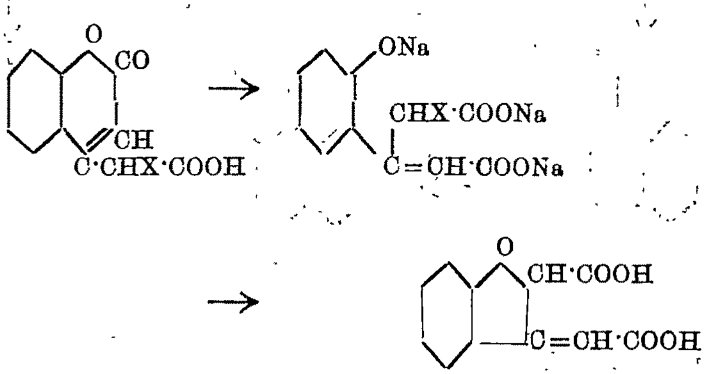


It is perfectly certain, therefore, that there is a sharp difference between β-naphthapyrone-4-acetic acid and all the other coumarin-4-acetic acids examined in this paper, this being the only instance in which the ethenoid group and not the active methylene group has been found to be attacked by the halogen. We have only to record this fact for the present and wait further observations before attempting to offer an explanation of this phenomenon.

We must in this connection correct an error which has found its way into literature regarding the nature of the product obtained by chlorinating 6-methylcoumarin-4-acetic acid (Dey, *J. Chem. Soc.*, 1915, **107**, 1635). The conditions of experiment were practically the same as those adopted by us, but although the melting points of the products agree closely with those obtained in the present investigation, the conclusion that they were 3-chloro derivatives is obviously wrong as they have now been definitely proved to be 6-methylcoumarin-4-chloroacetic acid and 6-methyl-4-chloromethylcoumarin respectively. The product (m. p. 244°) obtained by boiling this chloro-acid with alkali, too, is not the 2-carboxy-5-methylbenzfuran-3-acetic acid as recorded in literature (Dey, *loc. cit.*) but must now be regarded as a member of the isomeric dihydrofuran derivative having the following structure:

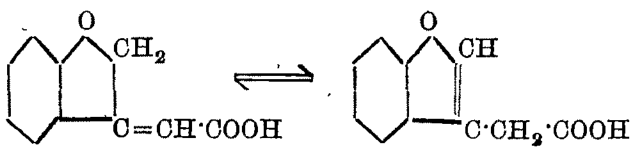


The formation of these dihydrofuran acids from the coumarin-4-chloro- and bromoacetic acids and from the 4-chloro- and 4-bromomethylcoumarins has been extensively studied and the mechanism of the reaction completely elucidated. By analogy to the action of alkali on 3-halogenocoumarins, the process is to be represented as follows:



They form dimethyl and diethyl esters readily, instantly decolourise alkaline permanganate and take up 2 atoms of hydrogen when reduced catalytically in the presence of platinum oxide. The 4-chloro- and 4-bromomethylcoumarins are similarly converted into unsaturated monocarboxylic acids (A).

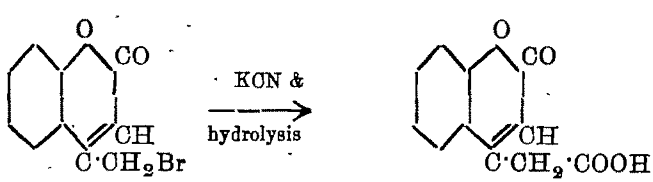
These yield monoalkyl esters and anilides and are readily hydrogenated to the saturated acids. The results of analyses and determination of molecular weights, as well as their chemical behaviour leave little room for doubt regarding the constitutions assigned to them and the mechanism of the reaction which gives rise to them. They have to be regarded as dihydrofuranone derivative and have been designated as 2-carboxydihydrofuranonyl-3-acetic acids and dihydrofuranonyl-3-acetic acids respectively. Attempts to convert them into the corresponding ketone or furanones by oxidation under various conditions were, however, unsuccessful, the molecules being completely broken up during the process. It is not improbable that the difficulty in getting the expected furanone arises from the presence of the characteristic glutaconic system which might cause a tautomerism of the following type in these acids.



(A)

Several unsuccessful attempts were made to confirm the constitutions of the 4-halogenomethylcoumarins and hence of the coumarin-4-halogenoacetic acids by other methods and a brief reference to some of the more important of these would not be out of place here.

The action of potassium cyanide was examined with the object of preparing the methocyanide, the subsequent hydrolysis of which to the coumarin-4-acetic acids might settle the constitution of the halogeno-4-methylcoumarins thus:



The reaction was presumably complicated by the simultaneous addition of the reagent to the double bond and no crystalline material could be isolated from the unpurifiable resinous mass which was always produced.

Several attempts were made to replace the halogen by OH, NH_2 and $C_6H_5 \cdot NH$ groups by treatment with appropriate reagents but

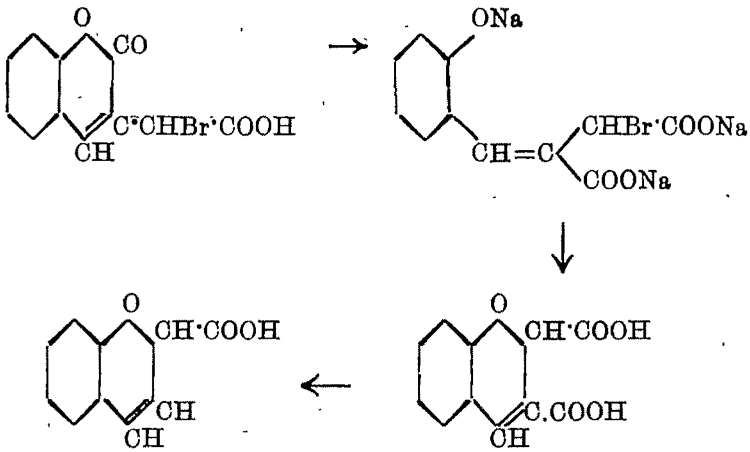
they were all unsuccessful. The halogen seems to be held very firmly and not a trace of it was removed even on heating with moist silver oxide at 100° for 8 hours. In contrast with this is the behaviour with aqueous alkali which eliminates the halogen completely in the course of a few minutes. The difference is obviously to be explained by the fact that the alkali does not initially attack the bromine but that it is the pyrone ring which is first opened up, the subsequent rearrangement to the stable benzodihydrofuran ring involving the interaction of the bromine and the phenolic hydrogen. The preparation of compounds of the Grignard type with magnesium in dry ether was also attempted without success.

The oxidation of the 4-halogenomethylcoumarins to the halogen-free salicylic and hydroxynaphthoic acids has, however, been successfully accomplished, almost theoretical yields being obtained by carrying out the oxidation with permanganate in acetone solution. Similarly, reduction with nascent hydrogen was found to succeed best on refluxing an aqueous acetone solution of the substance with zinc-copper couple, the corresponding 4-methylcoumarins being obtained in quantitative yield. Experiments are now in progress for synthesising these halogenomethylcoumarins by the condensation of phenols with γ-halogenoacetoacetic ester and thereby obtaining conclusive evidence of their constitution. The results will be communicated very shortly.

The monohalogenocoumarin-3-acetic acids are on the same grounds believed to be similarly constituted, the methylene hydrogen atom being replaced by halogen. These acids are very stable and cannot be decarboxylated in the usual way into the corresponding methochloride or methobromide. The oxidation to the halogen-free salicylic acids and reduction to the parent coumarin-3-acetic acids are, however, readily effected, and the halogen is as easily eliminated by boiling alkali as in the case of the corresponding 4-acetic acid derivatives. Attempts will be made to synthesise similar products from phenols and α-aceto-α'-chlorosuccinic ester.

The action of alkali on these acids is very interesting, the compounds formed being regarded as benzpyrane derivatives. A dicarboxylic acid should normally be produced, but one of the two carboxyl groups, most probably the one attached to position-3 which is known to be unstable, loses CO_2 and a monocarboxylic acid results. Analysis, molecular weight determination and the general

chemical properties of the acids are in complete agreement with the formula given.



EXPERIMENTAL.

The coumarin-4-acetic acids were prepared directly from citric acid by the method developed in an earlier investigation (Dey and Row, *J. Indian Chem. Soc.*, 1924, 1, 110).

7-Methylcoumarin-4-acetic acid.—9 G. of this acid (m. p. 190°), 4 g. of 4:7-dimethylcoumarin (m. p. 134°) and another product crystallising from acetic acid in stout needles (m. p. 210°) were generally obtained from a mixture of citric acid (24 g.), *m*-cresol (10 g.) and sulphuric acid (32+15 c.c.).

7-methylcoumarin-4-bromoacetic acid.—The uncrystallised acid (4 g.) was heated with a 50 % solution of bromine in glacial acetic acid (7 c.c.) on the boiling water-bath for about 45 minutes. There was copious evolution of HBr and the solution which became clear and almost colourless deposited on cooling 3·9 g. of crystals. The major portion of this dissolved in cold sodium bicarbonate leaving an insoluble residue which after washing with alcohol, weighed 1·5 g., m.p, 227-28°. The clear filtrate was carefully acidified with acetic acid, the turbid liquid filtered again and dilute hydrochloric acid added when the bromo acid slowly separated out, yield 2·3 g. Crystallisation from 60 % alcohol (charcoal) gave clusters of colourless rods, m.p. 228°. It is insoluble in water but dissolves readily in alcohol, acetic acid and other common organic solvents. (Found: C, 48·6; H, 2·84; M.W., 294·9. $C_{12}H_9O_4Br$ requires C, 48·5; H, 3·0 per cent. M.W., 297).

The *ethyl ester* was prepared by saturating the alcoholic solution of the acid with dry HCl, pouring into water, washing the precipitated solid with cold sodium carbonate and crystallising from alcohol. Colourless needles, m. p. 144°. (Found: C, 51·62 ; H, 3·97. $C_{14}H_{13}O_4 Br$ requires C, 51·69 ; H, 4·0 per cent).

The *methyl ester* separates from hot methyl alcohol in colourless stout needles, m. p. 162°. (Found: C, 50·07; H, 3·50. $C_{13}H_{11}O_4 Br$ requires C, 50·1 ; H, 3·54 per cent).

6-*Methyl-2-carboxydihydrofuranonyl-3-acetic acid.*—The bromo acid (2 g.) was boiled for an hour with caustic potash (6 g. in 20 c. c. water) and the clear yellow solution cooled and acidified. The white precipitate was purified by reprecipitating from a cold bicarbonate solution and crystallising twice from boiling water as colourless needles, m p. 231°, yield 1·4 g. The acid is very soluble in alcohol and acetic acid and sparingly soluble in hot water. It is quite stable and does not decompose at its melting point. (Found: C, 61·27 ; H, 4·32 ; M. W., 232·2. $C_{12}H_{10}O_5$ requires C, 61·55 ; H, 4·27 per cent. M. W., 234).

The *diethyl ester*, prepared in the usual way, separated from dilute alcohol in soft needles, m. p. 118°. (Found: C, 66·34 ; H, 6·12. $C_{16}H_{18}O_5$ requires C, 66·21 ; H, 6·21 per cent).

The *dimethyl ester* crystallised in slender needles, m. p. 83°. It is rather easily hydrolysed to the acid (m. p. 231°) by dilute alkail. (Found: C, 64·22 ; H, 5·22. $C_{14}H_{14}O_5$ requires C, 64·12 ; H, 5·34 per cent).

7-*Methyl-4-bromomethylcoumarin.*—(*a*) From the decomposition of 7-methylcoumarin-4-bromoacetic acid. The acid (1 g.) was heated to 225-30° until the melt became clear and free from bubbles. The product was washed with sodium carbonate and alcohol and finally crystallised from boiling acetic acid as shining plates, m. p. 236°.

(*b*) From the product of direct bromination of 7-methylcoumarin-4-acetic acid. The insoluble residue, m. p. 227-28° (*vide supra*) was found to be practically pure 7-methyl-4-bromomethylcoumarin. Crystallisation from acetic acid furnished colourless plates, m. p. 236° not depressed by admixture with the other product. The substance is remarkably stable and on heating sublimed in the cooler parts as fine needles. (Found: C, 52·30; H, 3·47; Br, 31·42. $C_{11}H_9O_2Br$ requires C, 52·2 ; H, 3·56 ; Br, 31·60 per cent).

6-*Methyldihydrofuranonyl-3-acetic acid.*—The clear yellow solution obtained on boiling the bromomethylcoumarin (1 g.) with 30 % KOH

(10 c. c.) was cooled in ice and acidified with dilute hydrochloric acid. The product separated out slowly in snow white needles, completely soluble in sodium bicarbonate. It dissolves readily in hot water and crystallises on cooling in silky needles, m. p. 107°. It dissolves in concentrated sulphuric acid with a deep brown colour and instantly decolourises dilute permanganate and bromine water in the cold. It is very stable and melts on heating to a clear liquid without decomposition ; after fusion with KOH and a few drops of water at 200° the acid is recovered unchanged. The barium, calcium and silver salts are sparingly soluble, while the methyl and ethyl esters are obtained as sweet smelling liquids insoluble in alkali. [Found: C, 69·31 ; H, 5·22 ; M. W., 189. $C_{11}H_{10}O_3$ requires C, 69·05 ; H, 5·26 per cent. M. W., 190. Ag (in silver salt), 36 21. $C_{11}H_9O_3$ Ag requires Ag, 36·85 per cent].

The *anilide* crystallised from hot alcohol as long needles, m. p. 161°. (Found: N, 5·53. $C_{17}H_{15}O_2N$ requires N, 5·3 per cent).

Catalytic reduction of 6-methyldihydrofuranonyl-3-acetic acid: 6-Methyldihydrofuran-3-acetic acid.—Freshly prepared platinum oxide (0·1 g.) was added to a solution of the acid (0·5 g.) in alcohol (25 c. c.) and the solution shaken in contact with pure hydrogen under slight pressure until there was no further absorption (90 c. c. in about 2 hours). After filtering the platinum oxide and distilling off the alcohol from the water-bath the residual solid was crystallised from hot water in colourless glistening plates, m. p. 130°. It does not declourise permanganate or bromine water instantaneously but only after standing for some time. (Found: C, 68·25 ; H, 6·29. $C_{11}H_{12}O_3$ requires C, 68·75 ;H, 6·25 per cent).

Reduction of 7-methyl-4-bromomethylcoumarin to 4:7-dimethylcoumarin.—Freshly made zinc-copper couple (2 g.) was refluxed for an hour with a solution of the bromocoumarin (1 g.) in acetone (50 c. c.) and the hot solution quickly filtered. The crystals which came down on cooling melted at 130° after two crystallisations from alcohol. It was proved to be identical with 4:7-dimethylcoumarin by a mixed m. p. determination.

Oxidation of 7-methyl-4-bromomethylcoumarin.—A solution of the bromocoumarin (1 g.) in acetone (200 c. c.) was warmed to 40° and finely powered potassium permanganate (1·3 g.) added in small quantities with vigorous shaking. The brown precipitate was filtered after 12 hours and washed twice with boiling water. The yellow filtrate, on acidifying with dilute hydrochloric acid slowly deposited the acid

which crystallised from hot water (charcoal) as colourless needles, m.p. 176°. The acid is very soluble in alcohol, sparingly so in water and gives a deep violet colour with ferric chloride. It was identified with *m*-cresotinic acid, m. p. 177°. (Found: M. W., 152·8. $C_8H_8O_3$ requires M.W., 152).

7-*Methylcoumarin-4-chloroacetic acid.*—A solution of 7-methylcoumarin-4-acetic acid (2 g.) in hot acetic acid (30 c. c.) was treated with a stream of chlorine (generated from 0·7 g. of permanganate) on a water-bath for half an hour, the clear cold solutions poured into water and the solid collected after 2 hours and treated with dilute sodium carbonate to separate the chloro acid from the chloromethylcoumarin formed by spontaneous decarboxylation. The chloro acid crystallised from alcohol in soft needles, m.p. 170° (decomp.), yield 1 g. The residue after melting solidified and then melted at 274°. On heating the chloro acid with 20% alkali it was converted into the same carboxydihydrofuranonylacetic acid (m.p. 231°) which had been obtained from the bromoacid. (Found: Cl, 13·82. M. W., 249·6. $C_{12}H_9O_4Cl$ requires Cl, 14·06 per cent. M.W., 252·5).

The *methyl ester* crystallises from dilute alcohol in colourless needles, m.p. 160°. (Found: C, 58·72; H, 3·98. $C_{13}H_{11}O_4Cl$ requires C, 58·53; H, 4·13 per cent).

The *ethyl ester* separates from alcohol in sheaves of needles, m.p. 158°. (Found: C, 60·02; H, 4·47. $C_{14}H_{13}O_4Cl$ requires C, 59·88; H, 4·63 per cent).

7-*Methyl-4-chloromethylcoumarin.*—The spontaneously decarboxylated product obtained during the chlorination (0·8 g.) crystallised from acetic acid in clusters of needles, m.p. 214°. Boiling alkali converted it into the 6-methyldihydrofuranonyl-3-acetic acid (m. p. 107°). (Found: Cl, 18·23. $C_{11}H_9O_2Cl$ requires Cl, 17·86 per cent).

6-*Methylcoumarin-4-bromoacetic acid*, prepared in the usual manner from 6-methylcoumarin-4-acetic acid, crystallises in needles, m.p. 168° (decomp.). On boiling with acetic acid and allowing to crystallise, a large amount of rectangular plates, m.p. 177°, were obtained. These were found to be the corresponding bromomethylcoumarin formed by decarboxylation, yield 1·5 g. from 4·2 g. of coumarin-acetic acid. (Found: Br, 26·4; M.W., 300·1. $C_{12}H_9O_4Br$ requires Br, 27·0 per cent. M.W., 297).

The residue insoluble in sodium carbonate obtained during bromination weighed approximately 1·1 g. Crystallisation from acetic acid gave rectangular plates, m.p. 177°. (Found: Br, 31 32. $C_{11}H_9O_2Br$ requires Br, 31·6 per cent).

6-Methyl-4-bromomethylcoumarin.—The *methyl ester* crystallised in thin needles, m.p. 170°. (Found: C, 50·32; H, 3·38. $C_{13}H_{11}O_4Br$ requires C, 50·1; H, 3·5 per cent). The *ethyl ester*, small needles, m.p. 146°.

Action of alkali on 6-methylcoumarin-4-bromoacetic acid: 5-Methyl-2-carboxydihydrofuranonyl-3-acetic acid.—This was prepared by the usual method and crystallised from water in snow-white needles, m. p. 244°. (Found: C, 61·18; H, 4·2. M.W., 235. $C_{12}H_{10}O_5$ requires C, 61·54; H, 4·2 per cent. M.W., 234). The *dimethyl ester*, m.p. 102°, and the *diethyl ester*, m.p. 182°, were prepared easily in the usual way.

5-Methyldihydrofuranonyl-3-acetic acid was prepared by boiling the bromocoumarin (m.p. 177°) with alkali. The acid crystallises from water in silky needles, m.p. 104°, and decolourises bromine water and permanganate instantly. (Found: M. W., 189·5. $C_{13}H_{10}O_3$ requires M. W., 190).

Oxidation of 6-methyl-4-bromomethylcoumarin was carried out with permanganate in acetone solution, the acidified filtrate being repeatedly extracted with ether, evaporated and the residue purified by dissolving in sodium carbonate and finally crystallising from water in colourless needles, m.p. 149°, identical in all respects with *p*-cresotinic acid.

6-Methylcoumarin-4-chloroacetic acid and 6-methyl-4-chloromethylcoumarin.—1·3 G. of the chloro acid and 0·3 g. of the chloromethylcoumarin were obtained from 2 g. of the acetic acid by chlorinating in the usual way. The chloro acid crystallises from alcohol in aggregates of slender needles, m.p. 162° (decomp.). (Found: M.W., 249·4. $C_{12}H_9O_4Cl$ requires M. W., 252·5). The chloromethylcoumarin crystallises from acetic acid in silky needles, m.p. 149°. (Found: Cl, 16·78. $C_{11}H_9O_2Cl$ requires Cl, 17·0 per cent). The chloro acid and the chloromethylcoumarin yielded with hot alkalis the dihydrofuranonyl derivative melting at 244° and 104° respectively.

The *methyl ester* crystallises in thin plates, m.p. 156°. (Found: C, 58·6; H, 3·92. $C_{13}H_{11}O_4Cl$ requires C, 58·5; H, 4·13 per cent).

The *ethyl ester* crystallises in long needles, m.p. 146°. (Found: C, 60·1; H, 4·83. $C_{14}H_{13}O_4Cl$ requires C, 59·9; H, 4·63 per cent).

7-Methoxycoumarin-4-bromoacetic acid, prepared from 7-methoxycoumarin-4-acetic acid, crystallises from alcohol in rectangular plates, m.p. 168° (decomp.). (Found: M.W., 314·3. $C_{12}H_9O_5Br$ requires M. W., 313). *7-Methoxy-4-bromomethylcoumarin* crystallises from

excess of boiling acetic acid in flat needles, m.p. 204°. (Found: Br, 29·53. $C_{11}H_9O_3Br$ requires Br, 29·74 per cent).

6-Methoxydihydrofuranonyl-3-acetic acid, prepared from the bromomethyl derivative by boiling with 2*N*-alkali, crystallises from hot water in small needles, m.p. 126°. (Found: M.W., 208·4. $C_{11}H_{10}O_4$ requires M.W., 206).

Coumarin-4-bromoacetic acid was obtained from coumarin-4-acetic acid in very poor yield, the main product being the bromomethyl coumarin. It crystallises from dilute alcohol in needles, m.p. 185° (decomp.). (Found: C, 47·1; H, 2·4; M.W., 286·2. $C_{11}H_7O_4Br$ requires C, 46·6; H, 2·5 per cent. M.W., 283). *4-Bromomethylcoumarin* crystallises from alcohol in needles, m.p. 176°. (Found: Br, 33·1. $C_{10}H_7O_2Br$ requires Br, 33·5 per cent).

Benzodihydrofuranonyl-3-acetic acid was prepared easily by boiling 4-bromomethylcoumarin with alkali for a few minutes. It crystallises from hot water in snow-white needles, m. p. 98°, instantly decolourising permanganate and bromine water. (Found: M. W., 174·4. $C_{10}H_8O_3$ requires M. W., 176).

α-Naphthapyrone-4-bromoacetic acid crystallises from alcohol in colourless plates, m. p. 190° (decomp.), yield 1·3 g. from 5 g. of the pyrone. (Found: C, 53·6; H, 2·6. M. W., 337·8. $C_{15}H_9O_4Br$ requires C, 54·0; H, 2·7 per cent. M.W., 333).

4-Bromomethyl-α-naphthapyrone, the main product of the bromination, weighed 8 g. It crystallises from excess of glacial acetic acid in pale yellow plates, m. p. 197°. (Found: Br, 27·48. $C_{14}H_9O_2$ Br requires Br, 27·66).

α-Naphthadihydrofuranonyl-3-acetic acid crystallises from dilute alcohol in colourless needles, m. p. 130°. The silver salt was analysed. (Found: Ag, 32·33. $C_{14}H_9O_3Ag$ requires Ag, 32·43 per cent).

Oxidation of 4-bromomethyl-α-naphthapyrone.—A solution of the bromo compound (21 g.) in acetone (120 c. c.) was treated with permanganate (2·2 g.) and the oxidation allowed to proceed at the laboratory temperature for a couple of hours. The product was worked up in the usual way. Fine needles, m. p. 187° not depressed by admixture with an authentic specimen of 1-hydroxy-2-naphthoic acid.

3-Bromo-βα-1:2-naphthapyrone-4 acetic acid.—The βα-1:2-naphthapyrone-4-acetic acid (5 g.) suspended in acetic acid was treated with bromine in the usual way. The product separated at first as an oil which subsequently solidified to a yellow crystalline mass com-

pletely soluble in sodium carbonate. Crystallisation from alcohol gave shining yellow needles, m. p. 188° (decomp.), yield 2·7g. (Found: C, 53·8; H, 2·81: $C_{15}H_9O_4$ Br requires C, 54·1; H, 2·7 per cent).

The *methyl ester* crystallises in soft needles, m. p. 172°. (Found: Br, 23·66. $C_{16}H_{11}O_4$ Br requires Br, 23·03 per cent). The *ethyl ester* crystallises in colourless rhombic plates, m. p. 139°.

3-*Bromo-4-methyl-βa-*1:2-*naphthapyrone*.—The bromoacetic acid was heated to 200° when the acid completely melted with effervescence. The solid residue was washed with sodium carbonate and crystallised from alcohol as colourless plates, m. p. 146°, not depressed by admixture with a specimen of 3-bromo-4-methyl-βa-1:2-naphthapyrone obtained by the direct bromination of the naphthapyrone.

2-*Carboxy-β-naphthafuran-*3-*acetic acid*.—The bromo acid was boiled for an hour under reflux with 2*N*-NaOH the clear alkaline solution cooled and acidified and the solid crystallised from alcohol as colourless rectangular plates, m. p. 252° (decomp.). It does not decolourise permanganate and bromine water instantly as in the case with the furanonyl acetic acids. (Found: M. W., 263·2. $C_{15}H_{10}O_5$ requires M.W., 270). On heating a pinch of the acid with resorcinol and sulphuric acid pouring into water and adding alkali bright green fluorescence is developed. The *dimethyl ester* crystallises from alcohol in square plates, m.p. 158°. The *diethyl ester* forms shining plates, m. p. 104°.

3-*Chloro-βa-*1:2-*naphthapyrone-*4-*acetic acid*, prepared by chlorination in the usual way, crystallises from acetic acid in yellow plates, m. p. 152° (decomp.), yield 1·5 g. from 2·5 g. of the acid. (Found: M. W., 291·6. $C_{15}H_9O_4$ Cl requires M. W., 288·5). The *ethyl ester* crystallises in plates, m. p. 134°.

3-*Chloro-4-methyl-βa-*1:2-*naphthapyrone*, obtained by heating the above acid to 160-73° crystallises from boiling alcohol in stout needles, m. p. 187°, not depressed by admixture with a specimen synthesised from β-naphthol and α-chloroacetoacetic ester by Pechmann's method.

The chloro acid and the 3- chloronaphthapyrone were converted by hot alkali into the carboxyfuranacetic acid (m. p. 252°) and the furancarboxylic acid (m.p. 242°) respectively. The latter was mixed, however, with the coumarinic acid (m. p. 149°).

Coumarin-3-bromoacetic acid.—Comarin-3-acetic acid (4 g.), suspended in glacial acetic acid (15 c.c.) was treated with a 50% solution of bromine in acetic acid (7 c. c.) in the usual way. The resulting solid consisted entirely of the bromoacetic acid. It crystallises from acetic acid in glistening plates, m. p. 200°. The acid is remarkably stable and shows no signs of decomposition when heated considerably above its melting point. (Found: C, 46·1; H, 2·6; M. W., 279·7. $C_{11}H_7O_4Br$ requires C, 46·64; H, 2·5 per cent. M. W. 283·0).

The *methyl ester* crystallises in colourless needles, m. p. 94°. (Found: C, 48·5; H, 3·21. $C_{12}H_9O_4Br$ requires C, 48·5; H, 3·03 per cent).

Benzopyran-2-carboxylic acid.—The bromoacetic acid (2 g.) was boiled for half an hour with 2*N*-KOH and the colourless potassium salt which slowly separated out was dissolved in water. The solid obtained on acidification crystallises from dilute alcohol in rectangular plates, m. p. 142°. It does not decolourise immediately bromine or permanganate. (Found: C, 68·0; H, 4·71. $C_{10}H_8O_3$ requires C, 68·2; H, 4·55 per cent). The silver salt was analysed. (Found: Ag, 37·81. $C_{10}H_7O_3Ag$ requires Ag, 38·16 per cent).

PRESIDENCY COLLEGE,
MADRAS.

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A Note on Powell and Whittaker's Method for the Determination of Pentosans.

By T. S. Krishnan.

The pentosan content of substances is generally determined by distilling with dilute hydrochloric acid, either directly or in a current of steam and estimating the furfural that distills over. Several methods have been proposed for the determination of the furfural in solution. Amongst the most important are:—

(1) *The official method.* (" *Methods of Analysis of Association of Official Agricultural Chemists*" 1930, 3rd Edn., p. 284). The furfural is condensed with phloroglucinol in acid solution and the furfural-phloroglucide filtered, washed, dried and weighed. From this weight, the amount of furfural is calculated by using Kröber's tables.

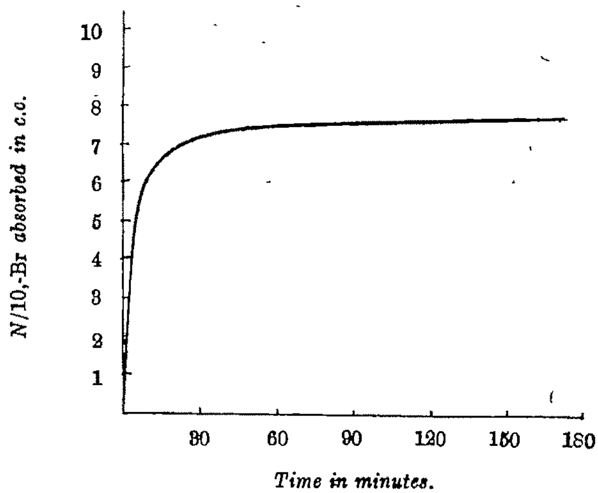
(2) *The bromine absorption method,* in which the furfural is allowed to react with bromine, when each molecule of furfural absorbs four atoms. From the amount of bromine absorbed the quantity of furfural is calculated according to the above reaction.

Pervier and Gertner (*Ind. Eng. Chem.*, 1923, **15**, 1167, 1255) in an elaborate review of the previous literature, have condemned the various methods for various reasons and have recommended the bromine absorption method to be the best. Even in this case, they failed to get satisfactory results when excess of bromine was employed. Hence they use only the exact amount of bromine required, the end point being determined electrometrically. Their procedure is somewhat tedious. The author has also found the official phloroglucinol method highly unsatisfactory for small quantities, whereas the bromine absorption method gave very satisfactory results. Powell and Whittaker (*J. Soc. Chem. Ind.*, 1924, **43**, 35 T) have employed excess of bromine and obtained good results. Deshpande (*J. Indian Inst. Sci.*, 1930, **13A**, 110) after a comparative study of several methods, concludes that the bromine absorption method gives the best results. More recently, after the author had finished all his work, Kline and Acree (E. S. R., 1932, **67**, 364) also conclude that the excess bromine titration method is speedy and accurate over wide ranges of concentration. When Powell and Whittaker's

method was employed by the author erratic results were obtained. Lack of proportionality in bromine absorption with varying concentrations of bromine in the reaction mixture was noticed. This defect was eventually traced to the influence of temperature and when the temperature was regulated highly satisfactory and very concordant results were obtained.

The improved bromine absorption method (*vide infra*), besides giving very accurate and concordant results, even when only very small quantities of furfural are present, is also far simpler to manipulate, especially when a large number of determinations have to be made than the official phloroglucinal method.

Fig. 1.



Experimental.

As the result of preliminary titrations the time of bromination was fixed at 90 minutes (Fig. 1).

Preliminary titrations, carried out according to Powell and Whittaker, showed that bromine absorption became relatively less as the concentration of furfural in solution increased (Table I).

TABLE I.

Influence of concentration of furfural and bromine in the reaction mixture.

$N/10$-Br_2 used.		Furfural solution used 5 c.c.	10 c.c.	15 c.c.	20 c.c.
20 c.c.	$N/10$-Br_2 absorbed				
30	by total furfural	3·85 c.c.	7·55 c.c.	10·60 c.c.	13·45 c.c.
20	Do	3·90	7·70	11·25	14·55
30	per c.c. of furfural	0·77	0·75	0·71	0·67
	Do	0·78	0·77	0·75	0·73

The above table shows that with the same initial concentration of bromine there is a progressive decline in the absorption with an increase in the furfural concentration. It also proves that with an increase in the initial bromine concentration there is an increase in the absorption, the concentration of furfural remaining the same.

Preliminary titrations also showed that the bromine absorption was influenced considerably by a temperature factor. A standard solution of furfural was prepared and the bromine absorption of equal quantities was measured at two different temperatures. The figures are given in Table II.

TABLE II.

Influence of temperature on bromine absorption of furfuraldehyde.

Quantity of furfural used.	$N/10$-Br_2.	Br_2 absorbed at 15° by Total soln.	per c.c.	Br_2 absorbed at 30° by Total soln.	per c.c.
5 c.c.	25 c.c.	3·50 c.c	0·70 cc.	3·70 c c.	0.74 c.c.
10	,,	6·70	0·67	7·50	0·75
15	,,	9·25	0·62	11·30	0·75
20	,,	11·55	0·58	14·90	0·75
15	50	10·70	0·71	11·20	0·75
20	,,	13·50	0·68	15·00	0·75

From the above table the following points are noted :—

(1) At the higher temperature absorption is greater.

(2) At the higher temperature absorption is quite proportional to the amount of furfural, the initial bromine concentration being the same in all cases.

(3) At the lower temperature absorption is not proportional to the amount of furfural, the relative absorption decreasing with the increase in concentration of the same.

(4) The absorption at 15° using 50 c. c. of bromine is distinctly higher than that obtained with 25 c.c. But even 50 c. c. of bromine at this temperature do not raise the absorption up to the 30° level. On the other hand, working at 30° this very large excess of bromine (50 c.c.) do not raise the absorption above that obtained with only 25 c.c.

To ascertain the optimum temperature of bromination an accurate standard solution of very pure furfural was prepared and the bromine absorption of equal quantities with identical bromine concentrations was measured at different temperatures. The results are given in Table III.

TABLE III.

Bromine absorption of furfural at different temperatures.
(1 C.c. furfural solution contains 0 0004565 g. furfural).

Standard furfural solution used.	$N/10$-Br_2.	$N/10$-bromine absorbed at. 15°	20°	25°	30°
5 c.c.	10 c.c.	0·90 c.c.	0·95 c.c.	0·95 c.c.	0.95 c.c.
10	10	1·80	1·99	1·85	1·90
25	10	3·95	4·35	4·60	4·75
50	20	8·05	8·80	9·40	9·55
50	50	9·00	9·45	—	9·55

From the above table it can be seen that 30° is the optimum temperature for bromination. At this temperature the bromine absorption is proportional to the concentration of furfural and is unaffected by variations in bromine concentration.

Further at 30° 10 c.c. of the furfural solution absorb 4·75 c.c. $N/10$-bromine. This corresponds to an absorption of 4 atoms of bromine by each molecule of furfural. Therefore by measuring the bromine absorption by a solution of furfural at 30° and by taking 1 c.c. of $N/10$ bromine to be equal to 0·0024 g. of furfural the accurate estimation of any furfural solution may be carried out.

The above experiments further show that at 30° a definite degree of bromination has been attained and this is not exceeded by increasing the bromine concentration even considerably.

At lower temperatures, especially with higher quantities of furfural, this degree of bromination was not attained by using quantities of bromine equal to those employed at 30°. In this case, however, an increase of bromine concentration was followed by increased absorption. It is remarkable that at 15° even a considerable increase of bromine concentration has failed to produce the degree of bromination attained at 30° with much lower bromine concentrations. The temperature factor is, therefore, most potent in this reaction.

Comparison of the phloroglucinol precipitation method and the modified bromine absorption method for small quantities of furfural.—A series of experiments were done to compare the relative accuracies of the above methods for small quantities of furfural.

A solution of pure furfural was prepared and used for all the following tests. Equal quantities were taken and estimated by the official precipitation method, a modified precipitation method and by the modified bromine absorption method. In the modified precipitation method, the precipitation is carried out in 200 c.c. instead of the 400 c.c., all the other conditions remaining the same. A correction of 0·0026 (being half the official correction for the 400 c.c. volume) was made. The results are given in Table IV.

TABLE IV.

Recovery of pure furfural by different methods.

Pure furfural taken.	Furfural found by		
	Phloroglucinol precipitation in		Bromine absorption at 30°.
	400 c.c. vol.	200 c.c. vol.	
0·00228 g.	0·00424	0·00302	0·00228
0·00456	0·00566	0·00496	0·00456
0·01140	0·01277	0·01142	0·01140
0·02280	0·02395	0·02390	0·02292

It is readily seen from the above figures that (*i*) the official method fails with small quantities, (*ii*) the modification improves it somewhat, (*iii*) the bromine absorption method gives very satisfactory results. At higher concentrations of furfural the official and the

bromine absorption method agree. A further proof of the failure of the official method for small quantities is given below.

In the determination of pentosans in a sample of fodder, the distillate was collected in four equal fractions of 300 c.c. each at intervals of an hour. They were separately tested for furfural content by the official phloroglucinol method and the bromine absorption method. The results are given in Table V.

TABLE V.

Comparison of the official and bromine absorption methods.

Distillation fraction.	Furfural as determined by Bromine absorption.	Phloroglucinol pption.
1	0·1375	0·1395
2	0·0144	0·0220
3	0·0079	0·0150
4	0·0054	0·0103
Total	0·1652	0·1868

This shows that the official precipitation method gives much higher values. With small quantities, the results are nearly 100% more than the bromine absorption method. Though there is likelihood of the bromine absorption figures being themselves slighlty higher, owing to the distillation of other bromine absorbing substances along with the furfural the official method gives far higher values and is, therefore, useless. This is due to the addition of the correction, which in these small quantities absolutely vitiates the result.

In another experiment, the distillate was collected in two fractions of 600 c.c. each and the furfural content was determined in each of the fractions separately and also after mixing in the entire distillate by both the methods. In this case, the phloroglucinol precipitation was done in 200 c.c. volume to minimise the errors (*cf.* Table VI).

TABLE VI.

Expt. No. 1.			Expt. No. 2.		
	Furfural as determined by			Furfural as determined by	
Distillation fraction.	Bromine absorption.	Phloroglucinol precipitation.	Distillation fraction.	Bromine absorption.	Phloroglucinol precipitation.
1	0·1213	0·1220	1	0·1300	0·1313
2	0·0277	0·0364	2	0·0169	0·0239
Total	0·1490	0·1584	Total	0·1469	0·1552
	0·1490	0·1360		0·1469	0·1328

Here also it can be seen that whereas the bromine absorption method gives concordant results, the precipitation method gives higher values in the separate fractions, but curiously enough gives lower values in the mixed entire distillate. In the first fraction, both the values agree while in the second the precipitation method gives nearly 50 % more in spite of the lower correction figure.

All the above data go to show the complete constancy and accuracy of the furfural estimations when carried out by the bromine absorption method at 30°.

SUMMARY

1. It is shown that at 30° the absorption of bromine by furfural is proportional to the quantity of the same irrespective of the bromine concentration in the reaction mixture, corresponding to the absorption of 4 atoms of bromine per molecule of furfural.

2. It is also shown that for small quantities of furfural the official method of precipitation with phloroglucinol fails to give accurate values, whereas the proposed bromine absorption method gives reliable figures.

It is a great pleasure to acknowledge the valuable help and guidance given by Dr. Warth during the course of this work.

ANIMAL NUTRITION SECTION,

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An Improved Check Valve for Vacuum Pumps.

By G. Narasimhamurthy.

It is a matter of common experience with vacuum pumps that even slight diminution in the rate of evacuation leads to the undesirable phenomenon of 'back-suction' often resulting in the spoilage of the experiments in progress. Moreover, the methods generally adopted for maintaining vacua are highly wasteful requiring continuous use of energy or constant flow of water often over several hours. There is need, therefore, for a proper safety devise that will eliminate (*i*) rise in pressure consequent on some possible defects in the evacuating system, and (*ii*) on the need for further evacuation after the desired condition is attained.

There are a few methods in common use for eliminating back suction but none of them would appear to be quite satisfactory. Among those which have been recommended, mention may be made of the use of (*a*) floating bobs (usually the section of a rubber stopper) enclosed in a cylindrical tube right above the passage that connects with the chamber under evacuation, and (*b*) simple valve arrangement by cutting a slit in the stopper (*Ind. Eng. Chem.*, 1923; **15**, 82). Both the above mentioned traps were tried by the author but found to be unsatisfactory.

The following is the description of the new check valve which can be made from materials found ordinarily in any laboratory. A fairly stout cyclindrical glass tube (A) diameter of 3-4 cm. is drawn at one end (Fig. 1) into an L-shaped tube, the narrower end of

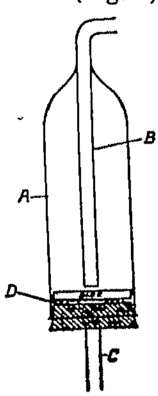

Fig. 1.

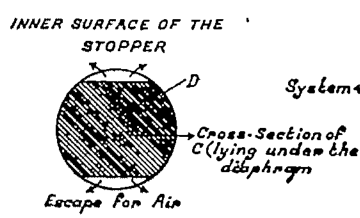

Fig. 2.

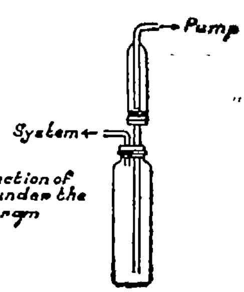

Fig. 3.

which will be connected to the suction pump. The other end is closed with a one-holed rubber-stopper; a tube (C) (diamater about 6 mm.) is passed through the stopper and pushed in just upto the surface without protruding into the space above. Covering the major portion of the surface of the same stopper is a thin strip of rubber (D) which is fixed in position with an adhesive. The position of the strip is indicated by the shaded portion in Fig. 2. Tube (B) which may be either fused in or fixed in position by a small rubber tube will be particularly useful, when a water pump is used. It helps to remove quickly any water that may collect on the top of strip D.

The valve thus prepared is mounted on a bottle which helps to keep it in a vertical position (Fig. 3). Where the valve is intended to maintain a very high vacuum (as when a Hyvac pump is used) a heavy metallic disc of diameter just wider than that of (A) and weighing about 100 g. will be useful in making the diaphragm settle evenly over the hole and thus effectively sealing the vacuum.

In actual use, this valve comes next to the pump so that when the pump is disconnected, the reduced pressure in the evacuated portion is maintained. Repeated trials have shown that once the required vacuum is attained, the pump can be disconnected without any rise in pressure and the reduced pressure maintained for several days.

The author's thanks are due to Professor V. Subrahmanyan, for for his interest and helpful suggestions in the above investigation.

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Glutathione as an Inductor in the Oxidation of Glucose.

By C. C. Palit and N. R. Dhar.

Hopkins (*Biochem. J.*, 1921, **15**, 286 ; 1925, **19**, 787 ; *J. Biol. Chem.*, 1922, **54**, 527 ; 1927, **72**, 185) and his pupils notably Harrison (*Biochem. J.*, 1924, **18**, 1009), Dixon (*Nature*, 1929, **124**, 512), Meldrum (*Biochem. J.*, 1930, **24**, 472, 1421) and others were successful in oxidising amino acids, proteins and fats by air in presence of glutathione. They were, however, unable to oxidise carbohydrates in the same manner.

It is of interest to note that roughly two-thirds of the body energy necessary for human life are obtained from the slow combustion of glucose and as the glutathione content of muscles, where animal oxidation is assumed to take place with the highest speed, is small, it can be concluded that glutathione is not the chief catalyst or inductor responsible for carbohydrate oxidation. The glutathione content of different organs is highest in liver (0·21%), in kidney 0·14% and least in muscle (0·05%).

In continuation of our work on induced oxidation of glucose in presence of insulin (Dhar and Dube, *J. Phys. Chem.*, 1932, **36**, 444), we have carried on experiments on the induced oxidation of glucose in presence of glutathione. We have observed that dilute bromine water can oxidise glutathione solutions without affecting glucose. In all the experiments described in this paper, the glutathione was first oxidised by the addition of dilute bromine water before the glucose was estimated by Fehling's solution. The experimental results show that contrary to the existing opinion, glutathione in solution can induce the oxidation of glucose by air at the ordinary temperature.

Experimental.

All the experiments were carried out at the laboratory temperature of about 25°. In these experiments, a slow current of air was passed through a series of bottles containing 50% caustic potash solution, baryta solution and concentrated sulphuric acid to free the air from

carbon dioxide and bacteria. A measured volume of this carbon dioxide-free air was passed for a definite time through the solution of glucose containing glutathione and other substances such as ferrous hydroxide, cerous hydroxide, cupric hydroxide, manganous hydroxide, sodium phosphate, etc. The glutathione used was obtained from the British Drug Houses, London, and the p_H of 0·05 % solution was 5·5, and did not reduce Fehling's solution. Extra pure glucose from (Merck) was used for the experiments. The volume of the solution to be oxidised was always made up to 100 c. c. by adding distilled water. The p_H of the mixture after oxidation did not materially differ from the p_H before oxidation.

TABLE I.

Glutathione added.	Air passed.	Duration of air passed.	Amount of glucose oxidised in presence of solution of sodium phosphate containing in g. 0·00 (=0 c. c.)	0·1440 (=10 c. c)	0·2880 (=20 c. c.)	0·4320 (=30 c. c.)
0·00 g.	18·0 litres	9 hrs.	0·5 %	8·7 %	4·4 %	6·1 %
0·00	36·5	9	0·8	...	9·2	...
0·00	73·0	30	...	...	15·54	...
0·05	18·0	9	2·8	11·2	13·0	15·1
0·05	36·5	9	4·4	...	15·6	...
0·05	73·0	30	...	...	50·9	...
0·10	18·0	9	4·0	13·5	...	28·1

TABLE II.

Vol. of air passed = 18 litres during 9 hrs.

Substances used.	Amount added.	Amount of glucose oxidised in absence of glutathione.	in presence of glutathione (=0·05 g)
Sodium carbonate	0·10 g.	29·7 %	14·0 %
,, bicarbonate	0·10	8·5	8·8
,, sulphite	0·10	15·2	12·2

The results recorded in Tables II and I show that in presence of glutathione, glucose is appreciably oxidised by passing air, and in presence of phosphate the amount of oxidation is increased. It seems that glutathione acts as an inductor in the oxidation of glucose in presence of phosphate. It is well known that the part which

phosphate plays in the animal metabolism is unique. Moreover, when the amount of air or glutathione is increased, the amount of oxidation increases. In presence of sodium carbonate and sodium sulphite, the induced oxidation of glucose in presence of glutathione is retarded.

In catalytic reactions a mixture of two or more catalysts is generally found to be more effective than their additive values. Moreover, in the animal body a group of inductors, *e.g.*, glutathione, internal secretions, vitamins (ascorbic acid) and other reducing substances of blood (*cf. Annual Reports*, 1930, p. 267) seem to take part in inducing the oxidation of food materials. All these inductors are capable of taking up oxygen directly from the air at the ordinary temperature and the oxidation of the inductors possibly leads to the oxidation of the food materials. In order to find out whether the addition of inorganic inductors like ferrous hydroxide, cerous hydroxide to glutathione leads to the greater oxidation of glucose, the following experiments were carried out and results recorded below.

TABLE III.

Oxidation of glucose in presence of inductors, and $Ce(OH)_3$ *and* $Fe(OH)_2$.

$Ce(OH)_3$ = 0·1069 g. $Fe(OH)_2$ = 0·0468 g. 10 C.c. glucose solution = 0·2808 g. CuO.

		Cerous hydroxide			Ferrous hydroxide		
Air passed (litres).	Duration. (hrs.).	Glutathione added.	Na-phosphate added in 20 c. c. of the solution.	Glucose oxidised.	Glutathione added.	Na-phosphate added in 20 c. c. of the solution.	glucose oxidised.
36·5	18	0·00 g.	0·0000 g.	41·7 %	0·00 g.	0·0000 g.	16·4 %
,,	,,	0·00	0·2880	56·9	0·00	0·2880	18·8
,,	,,	0·05	0·0000	22·3	0·05	0·0000	13·1
,,	,,	0·05	0·2880	80·4	0·05	0·2880	16·55
73·0	30	0·00	0·0000	78·76	0·00	0·0000	33·3
,,	,,	0·00	0·2880	80·3	0·00	0·2880	51·3
,,	,,	0·05	0·0000	65·9	0·05	0·0000	26·17
,,	,,	0·05	0·2880	68·5	0·05	0·2880	42·03

TABLE IV *a*.

Oxidation of glucose in presence of inductors, $Ce(OH)_3$ *and* $Fe(OH)_2$ *mixed with varying amounts of* $Cu(OH)_2$.

$Ce(OH)_3$ = 0·1069 g. $Fe(OH)_2$ = 0·0468 g. $Cu(OH)_2$ = 0·0094 to 0·00094 g. 10 C.c. of glucose = 0·2808 g. of CuO. Air passed = 73 litres in 30 hrs.

		Cerous hydroxide.		Ferrous hydroxide.	
$Cu(OH)_2$ added.	Glutathione added.	Na-phosphate added in 20 c. c. of the solution.	Glucose oxidised.	Na-phosphate added in 20 c. c. of the solution	Glucose oxidised.
0·0094 g.	0·00 g.	0·0000 g.	43·07 %	0 0000 g.	39·25 %
0·00094	,,	,,	84·9	,,	50·8
0·0094	,,	0·2880	71·6	0·2880	57·0
0·00094	,,	,,	86·5	,,	61·7
0·0094	0·005	0·0000	27·03	0·0000	34·57
0·00094	,,	,,	35·6	,,	44·0
0·0094	,,	0·2880	67·8	0·2880	55 0
0·00094	,,	,,	70·5	,,	56·1

TABLE IV *b*.

Oxidation of glucose in presence of inductors, $Ce(OH)_3$ *and* $Fe(OH)_2$ *mixed with minute amounts of* $Mn(OH)_2$.

$Ce(OH)_3$ = 0·1069 g. $Fe(OH)_2$ = 0·0468 g. $Mn(OH)_2$ = 0·00328 g. 10 C.c. of glucose soln. = 0·2808 g. of CuO(before oxidation). Air passed = 36·5 litres in 5½ hrs.

Inductors.	$Mn(OH)_2$.	Glucose left after oxidation in terms of CuO.	Glucose oxidised in terms of CuO.	Glucose oxidised.
Cerous hydroxide	0·0000 g.	0·1854 g.	0·0454 g.	19·67 %
,, ,,	0·00328	0·1306	0·1002	43·41
Ferrous hydroxide	0·0000	0·2208	0·0100	4·33
,, ,,	0·00328	0·1194	0·1114	48·26

TABLE V.

Oxidation of glucose in presence of mixed iuductors.

The principal inductor is $Ce(OH)_3 = 0{\cdot}1069$ g. or $Fe(OH)_2 = 0{\cdot}0468$ g., the minor inductors being a mixture of $Cu(OH)_2$ (0·00094 g.) with $Fe(OH)_2$ (0·00162) or $Ce(OH)_3 = 0{\cdot}0025$ g. in very small quantity. 10 C.c. of glucose solution = 0·2808 g. of CuO, and the volume of air passed = 73 litres in 30 hours. The minor inductors are put within brackets.

Glutathoine added.	Na-phosphate added in 20 c. c. of the solution.	Amount of glucose oxidised.	Glutathoine added.	Na-phosphate added in 20 c.c. of the solution.	Amount of glucose oxidised.
$Ce(OH)_3 = 0{\cdot}1069$ g.			$Fe(OH)_2 = 0{\cdot}0468$		
$Ce(OH)_3 + [Cu(OH)_2 + Fe(OH)_2]$			$Fe(OH)_2 + [Ce(OH)_3 + Cu(OH)_2]$		
0·00 g.	0·0000 g.	80·2 %	0·00 g.	0·0000 g.	81·2%
,,	0·2880	70·5	,,	0·2880	60·5
0·05	0·0000	47·3	0·05	0·0000	47·2
,,	0·2880	41·8	,,	0·2880	43·6

TABLE VI.

Oxidation of glucose in presence of small amount of inductors.

10 C. c. of glucose taken = 0·2808 g. of CuO. 73 litres air passed in 30 hrs.

TABLE VI.

	$Fe(OH)_2 = 0{\cdot}0032$ g.				$Ce(OH)_3 = 0{\cdot}005$ g.			
Glutathione added (g.) ...	Nil	Nil	0·05	0·05	Nil	Nil	0·05	0·05
Na-phosphate added in 20 c. c. soln. (g.) ...	Nil	0·2880	Nil	0·2880	Nil	0·2880	Nil	0·2880
Glucose oxidised (%) ...	19·5	21·5	57·8	85·9	16·7	17·8	46·5	49·3
	$Mn(OH)_2 = 0{\cdot}0038$ g.				$Cu(OH)_2 = 0{\cdot}00158$ g.			
Glutathione added (g.) ...	Nil	Nil	0·05	0·05	Nil	Nil	0·05	0·05
Na-phosphate added in 20 c. c. soln. (g.) ...	Nil	0·2880	Nil	0·2880	Nil	0·2880	Nil	0·2880
Glucose oxidised (%) ...	19·46	22·05	76·45	86·77	15·8	20·3	54·8	62·56

The results recorded in Tables III—VI show that the addition of glutathione to cerous or ferrous hydroxide acting as an inductor leads to a decrease in the induced oxidation of glucose. Similarly glutathione also retards the induced oxidation of glucose by mixture of inductors consisting of ferrous hydroxide and cupric hydroxide or cerous and cupric hydroxides. When, however, the amounts of cerous, ferrous, manganous or cupric hydroxide are small and vary from 0·005 to 0·00188 g., the addition of glutathione markedly increases the oxidation of glucose. Similar results have also been obtained in the induced oxidation of tartrates *in vitro*.

Moreover, we have observed that the addition of small amounts of manganese to cerous or ferrous hydroxide acting as inductors in the oxidation of glucose markedly increases the induced oxidation of glucose as will be evident from the results noted in Table IV*b*.

These observations *in vitro* are in agreement with those recorded in *vivo*. Hart, Steenbock, Waddell and Elvehjem (*J. Biol. Chem.*, 1928, **77**, 797) showed that the presence of minute amounts of copper is necessary for the utilisation of iron in the formation of hæmoglobin in the red blood corpuscles of the rat. The recent experiments of Orth, Wickwire and Burge (*Science*, 1934, **79**, 33) indicate that copper is likewise necessary for the formation of chlorophyll in the leaves of the orange trees. It is interesting to note that cattle grazing on certain types of Florida pasture land develop a nutritional anæmia, just as citrus fruit trees on certain lands become unhealthy and this may be cured by the use of iron and copper.

Simlar observations of Lipman and collaborators (*Plant Physiol.*, 1926, **1**, 231; 1931, **6**, 593) indicate that in the absence of minute quantity of copper the production of flowers is altered. Moreover, with barley in absence of small quantity of copper, not only flower and seed formation but also the growth are adversely affected. Recently Sommer (*ibid.*, p. 339) obtained poor growth with flax, tomatos and sun flower in the absence of copper but on adding 0·06 part of copper per million parts of the medium, 12 to 40 times as much green matter was produced.

In previous publications (Compare, Dhar, " New Conceptions in Biochemistry," 1932), we have shown that the addition of nitrogenous substances like glycine and alanine or salts of fatty acids like potassium stearate or oleate, retards the induced oxidation of glucose. In the following table, we have recorded the results on the induced oxidation of glucose due to the inductors like ferrous or cerous hy-

hydroxide in presence of glycine or potassium oleate to which glutathione has been added in some cases.

TABLE VII.

Oxidation of glucose mixed with (a) *glycine and* (b) *potassium oleate in presence of inductors,* $Ce(OH)_3$ *and* $Fe(OH)_2$.

10 C.c. of glucose = 0·2308 g. of CuO. 36·5 litres of air passed during 13 hrs.

Ce $(OH)_3$ used = 0·106 g.

	glycine added = 0·1 g.				K-oleate added = 0·1 g.			
Glutathione (g.)...	Nil	Nil	0·05	0·05	Nil	Nil	0·05	0·05
Na-phosphate (g.)...	Nil	0·2880	Nil	0·2880	Nil	0·2880	Nil	0·2880
Glucose oxidised (%) ...	18·3	31·45	8·2	37·6	14·6	19·5	11·4	25·6

$Fe(OH)_2$ used = 0·0468 g.

	Glycine added = 0·1 g.				K-oleate added = 0·1 g.			
Glutathione (g.)...	Nil	Nil	0·05	0·05	Nil	Nil	0·05	0·05
Na-phosphate (g.)...	Nil	0·2880	Nil	0·2880	Nil	0·2880	Nil	0·2880
Glucose oxidised (%) ...	24·3	49·6	14·4	66·55	41·4	43·5	34·3	45·3

The above table shows that in the absence of phosphate, glutathione appreciably retards the induced oxidation of glucose using ferrous or cerous hydroxide as the main inductor ; but in presence of phosphate, glutathione accelerates this induced oxidation of glucose.

Experiments in Sunlight.

TABLE VIII.

Vol. of air passed = 18 litres during 9 hours. Temp = 47°.

Glutathione added.	Amount of glucose oxidised in presence of phosphate containing in g.			
	0·0000 (= 0 c. c.)	0·1440 (= 10 c. c.)	0·2880 (= 20 c. c.)	0·4320 (= 30 c.c.)
0·00 g.	2·0%	9·7%	13·0%	18·6%
0·05	3·4	14·3	22·7	28·2
0·10	6·0	17·8	—	—

TABLE IX.

Vol. of air passed = 25 litres during 7 hours. Temp. = 47°.

	Photosensitiser.	Amount used.	Amount of glucose oxidised in absence of glutathione.	Amount of glucose oxidised in presence of glutathione. (=0·05 g.)
1.	Zinc oxide	0·50 g.	17·7%	27·4%
2.	Uranium nitrate	0·50 g.	96·2	99·0
3.	,, ,,	0·10 g.	86·1	89·1
4.	Ferric nitrate	0·10 g.	77·9	88·3
5.	Animal charcoal	0·50 g.	4·5	5·8

TABLE X.

Vol. of air passed = 18 litres during 9 hours. Temp. = 47°.

Substance used.	Amount used.	Amount of glucose oxidised in absence of glulathione.	Amount of glucose oxidised in presence of glulathione. (=0·05 g.)
Sodium carbonate ...	0·10 g.	41·3%	29·3%
,, bicarbonate ...	0·10	23·5	32·5

The above results show that in presence of sunlight, the induced oxidation of glucose in presence of glutathione is increased. Photosensitisers markedly accelerate the reaction, whilst animal charcoal is a poor accelerator. It appears, therefore, that sunlight is of importance in enhancing the oxidation of glucose *in vitro* as well as in the animal body.

F. G. Benedict ("The Physiology of Large Reptiles," Carnegie Institution of Washington, 1932, p. 514), has expressed the opinion that the relatively low heat production with cold-blooded animals in comparison with the warm-blooded animals of the same size is due to the difference in the distribution of the blood carrying the three important factors of metabolism, *viz.*, oxygen, nutrients and hormones and that increased blood flow is associated with increased metabolism. In the cold-blooded animals the amount of blood is relatively less than in warm-blooded animal. The heat production in the body

seems to be controlled by the blood supplied to the tissues. Where there is a liberal blood supply to the tissues, the heat generation can be high ; where the blood supply is low the heat production must be low also. The blood distribution is not determined by the metabolism, because with man the same blood distribution may permit his metabolism to be increased 1000% in extreme cases. Lusk ("Science of Nutrition," 1919, p. 105) has stated that in starvation, amongst the various body organs, the greatest loss in weight is suffered by the glands and their activity is greatly reduced. Taking the above points in consideration, it seems likely that the internal secretions acting as inductors largely control animal oxidation. In starvation, the amount of internal secretion available for accelerating the oxidation decreases and hence the metabolism is decreased. In violent exercise, the metabolism is highly increased probably due to the increase in the oxygen intake and a greater supply of internal secretions from the various glands. It appears that although glutathione and other reducing agents present in the blood are of some importance in animal metabolism, the chief inductor seems to be the internal secretions.

Summary.

1. Glucose is appreciably oxidised by air at the ordinary temperature in presence of glutathione. The amount of oxidation increases when phosphates are added.

2. In presence of small amounts of cerous, ferrous, manganous or cupric hydroxide, the addition of glutathione markedly increases the oxidation of glucose. Similarly the addition of small quantities of manganese to cerous or ferrous hydroxide increases the induced oxidation of glucose.

3. The induced oxidation of glucose in presence of glutathione is accelerated by light and photosensitisers further accentuate the reaction.

4. There is no correlation between the glutathione content of animal tissues and the intensity of metabolism. It seems that internal secretions acting as inductors largely control animal oxidation.

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Determination of Parachor in Solution. Part I.

By Susil Kumar Ray.

The determination of parachor at the present time has helped to solve many intricate and difficult problems of structural chemistry. The main drawback of the method is its limitations in the case of the liquid or fused state of matter only. There are substances of very high melting points, as well as compounds which decompose on fusion, the determination of parachors of which is either difficult or impossible. To get over this difficulty the present investigation was undertaken to find out the applicability of the straight line mixture law in the determination of parachor of solids dissolved in liquids. An attempt was made by Hammick and Andrew (*J. Chem. Soc.*, 1929, 754) to determine parachor of substances in solution. They considered a few simple binary liquid mixtures, and had shown that in solution parachor obeys the simple mixture law. No systematic investigations appear to have been made in this direction except a few isolated cases. In the present paper the surface tension and the density of the pure solvent as well as those of the solutions were determined and from a knowledge of the parachor of the former that of the solute was calculated, on the assumption that parachors obey the straight line mixture law.

The surface tension was determined by the method of maximum bubble pressure; the apparatus employed being of the usual Sugden type. The determination of parachors in solutions, particularly in dilute solutions, requires that all experimental data should be as accurate as possible. All the substances used were, therefore, very carefully purified by distillation or repeated crystallisation. Pressure differences were read correct to 0·08 mm. and the error is probably not more than 0·01 mm. Three bubblers were employed for every observation and five readings were taken with each. The surface tension was calculated from the mean of these fifteen readings. The bubblers were restandardised before each mixture was investigated. Densities were determined by means of a 10 c.c. specific gravity bottle.

The parachor of the solute was calculated from the following relations, as in the work of Hammick and Andrew (*loc. cit.*).

$$P_m = M_m \cdot r^{\frac{1}{4}} / D$$
$$P_m = P(1-x)P_x.x$$
$$M_m = M_s(1-x)M_x.x$$

where r and D are the surface tension and density of the solution, P_m, P and P_x are the parachors of the solution, solvent and the solute respectively, while M_m, M_s and M_x are the respective molecular weights and x is the molecular fraction of the solute.

In the present paper data are given for seventeen different solutions. The solutes examined were simple organic ring-compounds in order to find out the effect of ring structure on the parachor contribution as well (*cf.* Ray, *J. Indian Chem. Soc.*, 1934, **11**, 499). The solvents employed were both associated and non-associated, of every possible type with widely different chemical nature, so that any effects due to surface adsorption might be detected.

It will be seen from the following tables that the determination of parachor of the solute in solution agrees very closely, with a few exception, with the values either calculated or determined in the fused state. The agreement is most complete generally in very dilute solution and is dependent on the concentration of the solution. In this connection it is to be noted that in liquid mixtures the values are generally independent of the concentration of the solution as is evident from the work of Hammick and Andrew (*loc. cit.*). It is also of much interest to note that in the present series, the surface tension is increased by the dissolution of a solid in the liquid. In liquid mixtures the contrary is generally found to be the case (*cf.* Hammick and Andrew, *loc. cit.*).

It will be found that abnormal results were obtained in three cases, *viz.*, naphthalene in chloroform and phenanthrene in acetone and in carbon tetrachloride. In the case of phenanthrene in acetone the value is found to be lower by about 60 units, while in the other two cases the values are higher by about 20 and 50 units. It is presumed that in these cases either association between the solute molecules or between the solute and the solvent molecules or some kind of dissociation is taking place. The small variations found in some cases are due probably to Gibb's surface adsorption effect.

In the following table, the parachor of the substances determined in the fused state, where possible, are given, so that the values determined in solution may be compared. The density was determined by means of a U-shaped pyknometer as employed by Sugden

Parachor in the Fused State.

TABLE I.

	Temp.	Density.	Surface tension.	$P_{obs.}$	$P_{calc.}$
Naphthalene	80·8°	0·9751	32·03	312·3 (312·5 B&S)	313·0
α-Naphthol	98·0	1·1130	40·02	329·4 (336·7 B&S)	333·0
Coumarin	99·8	1·1780	41·81	315·2	314·0
8-Oxyquinoline	98·5	1·1271	39·68	322·8	323·6
Phenanthrene	120·0	1·0370	36·34	420·4	418·0

Parachors of naphthalene and α-naphthol in the fused state have been determined by Bhatnagar and Singh (*J. Indian Chem. Soc.*, 1929, **6**, 263).

Parachor in Solution.

In the following tables x is the molar fraction of solute, M_m the the mean molecular weight of the solution, P_m the mean parachor and P_x, the parachor of the solute. Except a few cases the determinations of surface tension and the density were carried out between the temperature of 30-32°.

TABLE II.

Naphthalene in benzene.

x.	Density.	Surface tension.	$M_{m.}$	$P_{m.}$	$P_{x.}$	$P_{calc.}$
0·0	0 8681	27·38	78	205·5	...	
0·03101	0·8802	28·54	79·55	208·9	312·6	
0·04650	0·8847	28·89	80·32	210·5	311·1	
0·08569	0·8900	29·12	82·27	214·7	312·7	
0·09592	0·8946	29·46	82·79	215·6	310·7	
					mean 311·8	313·0

Table III.
Naphthalene in carbon tetrachloride.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	1·5920	26·55	153·83	219·3	...	
0·03746	1·5576	26·65	152·80	222·7	312·3	
0·05480	1·5429	26·66	152·52	224·6	312·6	
0·08872	1·5232	27·10	151·57	227·3	311·1	
0·1089	1·5094	27·51	151·04	229·2	310·2	
				mean	311·6	313·0

Table IV.
Naphthalene in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	1·4701	26·37	119·37	184·1	...	
0·03461	1·4472	27·46	119·73	189·4	338·1	
0·06218	1·4185	27·35	119·95	193·4	333·4	
0·07187	1·4179	28·02	120·08	194·9	334·7	
				mean	335·4	313·0

Table V.
a-Naphthol in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·0	0·9718	35·52	79	198·5	...	
0·02983	0·9814	36·40	80·95	202·6	335·4	
0·03927	0·9857	35·71	81·57	203·7	333·6	
0·04932	0·9876	36·99	82·21	205·3	334·6	
				mean	334.5	333·0

Table VI.
a-Naphthol in ethyl acetate.

x.	Density.	Surface tension.	M_m	P_m.	P_x.	$P_{calc.}$
0·0	0·8885	22·66	88	216·1	...	
0·02453	0·8964	23·22	89·38	218·9	331·7	
0·03639	0·9014	23·71	90·04	220·4	332·6	
0·07962	0·9185	24·51	93·47	224·1	316·5	
0·1237	0·9350	25·17	94·91	227·4	308·1	333·0

TABLE VII.

Coumarin in benzene.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·04542	0·8881	28·24	81·09	210·5	314·8	
0·05772	0·8950	28·57	81·93	211·6	311·9	
0·1234	0·9278	29·45	86·39	216·9	297·4	314·0

TABLE VIII.

Coumarin in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·05693	1·4404	26·99	120·91	191·4	312·6	
0·08420	1·4316	27·84	121·64	195·0	313·5	
0·1111	1·4253	28·69	122·32	198·6	315·1	314·3
					mean 313·7	

TABLE IX.

Coumarin in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·02830	0·9851	36·61	80·58	201·2	313·6	
0·06197	0·9952	37·02	83·14	205·8	316·3	
0·09931	1·0092	38·03	85·65	210·9	323·4	314·0

TABLE X.

8-*Oxyquinoline in benzene.*

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}
0·01810	0·8805	28·31	79·23	207·6	320·3	
0·02238	0·8838	28·61	79·50	208·1	321·8	
0·03215	0·8886	28·81	80·16	209·0	323·4	
0·04889	0·8952	29·26	81·28	211·2	322·8	
					mean 322·08	323·6

TABLE XI.

8-Oxyquinoline in carbon tetrachloride.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·01748	1·5674	25·98	153·65	221·0	321·1	
0 02483	1·5637	26·00	153·60	221·8	322·2	
0·05498	1·5577	26·82	153·28	224·0	305·7	
0·09877	1·5295	27·20	153·02	228·4	311·9	323·6

TABLE XII.

Xanthone in chloroform.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·01799	1·4526	26·42	120·73	188·3	421·8	
0·03049	1·4513	27·01	121·68	191·2	419·8	
					mean 420·8	419·9

TABLE XIII.

Xanthone in pyridine.

x.	Density.	Surface tension.	M_m	P_m.	P_x.	$P_{calc.}$
0·01663	0·9803	36·11	80·95	202·3	420·7	
0·02749	0·9867	36·46	82·22	204·7	421·9	
					mean 421·3	419 9

TABLE XIV.

Phenanthrene in benzene.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·03308	0·8813	28·15	81·31	212·5	417·3	
0·05852	0·8926	28·95	83·85	217·9	417·0	
					mean 417·2	418·0

TABLE XV.

Phenanthrene in carbon tetrachloride.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	$P_{calc.}$
0·02452	1·5555	26·44	154·46	225·3	464·9	
0·03297	1·5503	26·90	154·59	227·2	469·2	
					mean 467·1	418·0

TABLE XVI.

Phenanthrene in acetone.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·0	0·7830	23·29	58	162 8	...	
0·02764	0·8065	23·84	61·32	168·0	351·0	
0·05230	0·8252	24·54	64·21	173·2	361·4	

TABLE XVII.

Anthracene in nitrobenzene.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·0	1·1928	43·06	123	264·1	—	
0·01091	1·1904	42·96	123·54	265·8	419·1	
0·01177	1·1893	42·83	123·59	265·9	416·5	
				mean	417·8	418·0

TABLE XVIII.

Dithiol thiodiazol in alcohol.

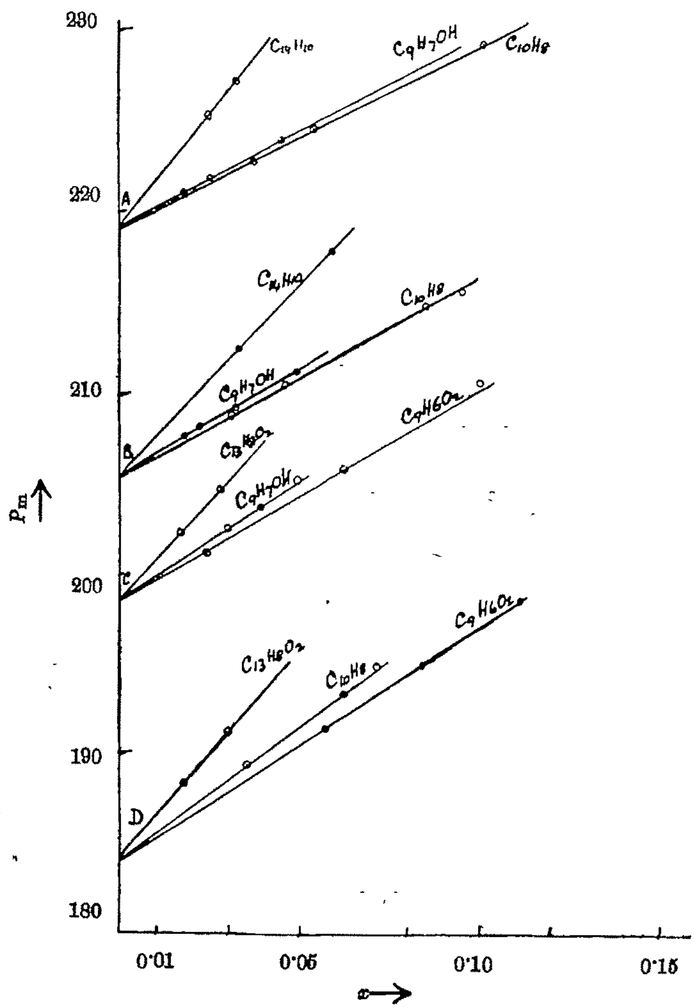
x.	Density.	Surface tension.	M_m.	P_m.	P_x.	P_{calc}.
0·0	0·7853	21·42	46	126·0	...	
0·01401	0·8038	22·22	47·46	128·0	264·2	
0·02752	0·8236	23·01	48·84	129·9	265·3	
				mean	264·8	267·7

It will be observed that the parachor values for α-naphthol in dilute pyridine and ethyl acetate solutions agree well with the calculated value 333; whereas in the fused state the substance gives a much lower value of 329·4. This is evidently due to some incipient decomposition or oxidation at the melting point. The red colour of the fused substance seems to support this idea.

It will be evident from the preceding tables that by the solution of a solid in a liquid the parachor of the mixture is increased and the increment of the parachor is proportional to the concentration of

the solution. This relation is somewhat similar to that observed by Raoult in the diminution of vapour pressure of the solvent by the dissolution of solids, and is best shown by the following curves obtained by plotting P_m against x. This is what can be expected considering the additive character of the parachor function.

FIG. 1.



A in CCl_4, B in C_6H_6, C in C_5H_5N & D in $CHCl_3$.

SUMMARY.

1. Parachor of simple ring compounds were determined in solution and it was found that parachor obeys the straight line mixture law in dilute solutions.

2. The values obtained in the solution are found to be dependent on the concentration of the solution.

3. By the dissolution of a solid in a liquid the resulting parachor of the mixture is increased over that of the solvent and the increment is proportional to the concentration.

4. The determinations of inorganic compounds in solution are under investigation.

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Resolution of Co-ordinated Inorganic Compounds into Optical Isomers. Part II. Resolution of Triethylenediaminozinc Chloride and Sulphate.

By Panchanan Neogi and Gopal Krishna Mukherjee.

The resolution of triethylenediaminocadmium salts into optical isomers has been described in Part I of this series (*J. Indian Chem. Soc.*, 1934, 11, 228). We have been able to resolve triethylenediaminozinc chloride and sulphate into optical isomers and isolate the *dextro* compounds in the solid state. As in the case of the triethylenediaminocadmium salts reagents like *d*-tartaric acid, *d*-camphor sulphonic acid, *d*-bromocamphor sulphonic acid, *d*-ammonium tartrate were at first tried, but all these reagents failed to resolve the zinc salts. Success was only achieved with *d*-sodiocamphor nitronate, as in the case of the cadmium salts. The *laevo* variety however, could not be isolated in the solid state though a *laevo*-rotatory solution was obtained by using nitrocamphor itself instead of the *d*-sodio salt. It is to be observed that sodiocamphor nitronate is *dextro*-rotatory whereas nitrocamphor itself is *laevo*-rotatory. Using the sodio salt, the *d*-components both in the case of the cadmium and zinc salts, were obtained in solutions from which acetone precipitated the *dextro* compounds in the solid state.

Using free nitrocamphor for the *laevo*-component the hydroxide of the co-ordinated zinc or cadmium salt was first prepared and combined with nitrocamphor and the resultant salt was fractionally crystallised. In the case of cadmium, the nitronate decomposed and could not be obtained in the pure state. In the case of the zinc salt, however, a *laevo*-rotatory camphor nitronate was obtained in the pure state which on fractional crystallisation yeilded a *laevo* compound with a maximum *laevo*-rotation. This compound was decomposed with dilute hydrochloric acid when the nitrocamphor separated out in the free state and filtered off and the solution was found to remain *laevo*-rotatory. Acetone or other

organic solvents, however, failed to precipitate the *laevo*-compound in the solid state. The solution, unlike nitrocamphor, soon racemised within a few hours. Details have heen given in the experimental.

Unlike cadmium salts, the *d*-bromide and *d*-iodide, which were obtained in solution, were not obtained in the solid state as acetone failed to precipitate them. The compositions and rotations of the tartrate, camphor sulphonate and bromocamphor sulphonate have been incorporated.

EXPERIMENTAL.

Triethylenediaminozinc tartrate.—A concentrated solution of triethylenediaminozinc chloride (8 g.) was triturated with silver tartrate (8 g.) prepared from a concentrated solution of Rochelle salt by precipitation with a concentrated solution of silver nitrate, washing with water and drying in a desiccator covered with black paper. The residue of silver chloride was repeatedly extracted with hot water. The extract was filtered and evaporated in vacuum. Various fractions of crystals were dried and all gave a constant nitrogen content. [Found: N, 19·01 ; Zn, 14·2. (Zn En_3). $C_4H_4O_6$, 3 H_2O requires N, 18·79 ; Zn, 14·5 per cent). Rotations of these substances were measured in a 2 dcm. tube and after four crystallisations the value of $[\alpha]_D^{31}$ for the first and the last fractions were +17 4° and +18·1° respectively. The values of α_D being +1·74° and +1·81° respectively with a 5% solution. This difference is not greater than the probable experimental error. The solutions showed no muta-rotation, for the rotations were found to be exactly the same even after 24 hours. The tartrate was converted to the corresponding chloride by means of barium chloride but in each case the resulting solution was inactive.

d-*Triethylenediaminozinccamphor sulphonate.*—To 200 C.c. of a solution of silver nitrate (15 g.) just sufficient caustic soda was added to precipitate all the silver as oxide ; this was washed with distilled water until free from alkali salts, filtered and the moist precipitate warmed with 150 c.c. of a solution of *d*-camphor sulphonic acid (20·5 g.). When the dissolution of the oxide was complete, the filtered solution was neutral to litmus. To a concentrated solution of recrystallised triethylenediaminozinc chloride (5 g.) the silver *d*-camphor sulphonate solution was added until the addition of one drop

more caused no further silver chloride to be precipitated. The solution was filtered, evaporated in vacuum and crystallised. It was recrystallised twice from water. [Found: N, 12; Zn, 8·80. $(ZnEn_3)$-$(C_{10}H_{15}O_4S)_2H_2O$ requires N, 11·5; Zn, 8·96 per cent.]. It was then subjected to fractional crystallisation. The rotations of the different fractions were measured in a 2 dcm. tube. After four crystallisations the values of the $[\alpha]_D^{34}$ for the first fraction and the last fraction were +16·5° and +18·1° respectively the values of α_D being + 1·65° and + 1·81° respectively with a 5% solution. The solutions showed no muta-rotation as their rotations did not change even on keeping them for 24 hours. On acidifying a concentrated solution of any of these fractions with hydrochloric acid and adding excess of acetone, the complex zinc chloride precipitated was found to be inactive.

d-*Triethylenediaminozincbromocamphor sulphonate.*—A solution of the silver salt of *d*-bromocamphor sulphonic acid was prepared in the same way as the silver salt of *d*-camphor sulphonic acid by dissolving silver oxide in a warm solution of *d*-bromocamphor sulphonic acid till a solution neutral to litmus was obtained. To a solution of triethylenediaminozinc chloride (5 g.) in water, the silver bromocamphor sulphonate solution, thus prepared, was added till the addition of one drop more caused no further precipitation of silver chloride. The solution was filtered and the residue of silver chloride was washed with hot water, filtrate evaporated in vacuum and fractionally crystallised and the different fractions purified by further crystallisations. Each of these fractions gave a constant nitrogen content. [Found: N, 9·02 ; Zn, 6·5. $(ZnEn_3)$ $(C_{10}H_{14}BrSO_4)_2,5H_2O$ requires N, 8·8 ; Zn, 6·8 per cent].

Rotations of the different fractions were observed in a 2 dcm. tube. The values of $[\alpha]_D^{34}$ for the first and the last fractions were 42° and 41° respectively with a 5% solution. On acidifying a concentrated solution of any of these fractions in water with hydrochloric acid and adding acetone in excess the complex zinc chloride was precipitated which was found to be quite inactive.

d-*Triethylenediaminocamphor nitronate.*—To a solution of triethylenediaminozinc chloride (6 g.) in water (20 c.c.) was added a solution of *d*-sodiocamphor nitronate (6 g.) in water (15 c.c) and the mixture well shaken. No precipitate appeared. The solution was evaporated in vacuum and three crops of crystals collected, The first

fraction was recrystallised from water when it appeared as colourless silky needles. This was completely free from chlorine. [Found: N, 16·91 ; Zn, 9·45 ; $(ZnEn_3)$ $(C_{10}H_{14}NO_3)_2$, 2 H_2O requires N, 16·6 ; Zn, 9·66 per cent].

Rotation of this substance was measured in a 2 dcm. tube and the value of the $[\alpha]_D^{35}$ was found to be +16° the value of α_D being +9·6° with a 3% solution and this rotation did not change on keeping it for 24 hours. The second and the third fractions on further purifications by crystallisation were found to have identical chemical composition and their specific rotations were +116·6° and +80·4° respectively under identical conditions, the actual rotations being +7·0° and +4·82° respectively with a 3% solution.

d-*Triethylenediaminozinc chloride.*—*d*-Triethylenediaminozinc-camphor nitronate (2 g.) (first fraction) was dissolved in the least quantity of water, and to the clear solution dilute hydrochloric acid was added drop by drop and shaken till all the nitrocamphor had precipitated out. The clear solution was filtered and the residue washed with a small quantity of water. To the filtrate excess of acetone was added when a perfectly white crystalline substance precipitated out which was allowed to settle. The supernatant liquid was then decanted off and the precipitate washed several times with acetone to remove all traces of the acid and any free nitrocamphor. The residue was quickly dried underneath a fan between filter papers. [Found: N, 26·62 ; Cl, 22·38; Zn, 20·40. $(ZnEn_3)Cl_2$ requires N, 26·58 ; Cl, 22·4 ; Zn, 20·67 per cent].

0·0898 G. of the substance was dissolved in 15 c.c. of water and a tube was completely filled with the solution (about 10 c.c.) when the rotation was found to be +0·5° which makes $[\alpha]_D^{35}=94·2°$ and $[M]=+297·6°$.

The activity of the solution rapidly diminished on keeping and almost completely vanished in 2-3 hours. The solid was, however, much more stable. Examined after an hour the specific rotation of the solid was found to be +50° and when kept cool and examined after three hours, the specific rotation fell to +20·5°, the actual rotations being +1·0° and +0·41° respectively with a 1% solution. Examined after 6 hours the salt was found to be quite inactive.

d-*Triethylenediaminozinc sulphate* was prepared in the same way as the chloride by decomposing the *d*-triethylenediaminozinccamphor nitronate with dilute sulphuric acid and precipitation with acetone. [Found: N, 24·75; Zn, 19·10; SO_4, 28·56. $(ZnEn_3)$ SO_4 requires

N, 24·63 ; Zn, 19·06 ; SO_4,28·14 per cent.]. Rotation of the substance was determined in a 2 dcm. tube with a solution of the concentration (·0518 g. in 15 c.c.) when the rotation was found to be +0·6° which makes $[\alpha]_D^{34} = +87{\cdot}7°$ and [M]=299 08°. The solution when examined after three hours was found to be quite inactive whereas the solid when kept cool and examined after 3 hours showed its specific rotation to be +16·2°, the value of α_D being +0·76° with a 25% solution but when examined after 6 hours was found to be quite inactive.

Triethylenediaminozinc camphornitronate.—A solution of triethylenediaminozinc chloride (5 g.) in water (15 c,c.) was triturated with moist silver oxide. The solution of the complex hydroxide was filtered and the residue washed with water and to the clear alkaline filtrate thus obtained nitrocamphor was gradually added (6 g. in all) with constant stirring whereby all the nitrocamphor almost dissolved The solution was then filtered and evaporated in vacuum when a tarry mass containing some crystalline substance was obtained which on repeated crystallisation was separated from the tarry matter. The substance was then fractionally crystallised. The first fraction was found to have a specific rotation of −42·6° the actual rotation being −2·56° with a 3% of solution examined in a 2 dcm. tube. The rotation of this substance also did not change on keeping. It was found to have identical chemical composition with that of the *dextro* variety.

l-*Triethylenediaminozinc chloride in solution.*—The *laevo*-triethylenediaminozinccamphor nitronate crystals (1 g.) were dissolved in water (15 c.c) and dilute hydrochloric acid was added drop by drop when nitrocamphor was found to precipitate out which was filtered off. The rotation of the solution was observed in a 2 dcm. tube when it was fonnd to be −1·16° but it completely racemised in an hour and a half. On adding acetone in excess no precipitate of the active substance could be obtained. The preparation of other salts is in progress.

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4-Bromomethylcoumarins. Synthesis from Phenols and γ-Bromoacetoacetic Ester.

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It has been shown in an earlier investigation (Dey and Radhabai, *J. Indian Chem. Soc.*, 1934, **11**, 685) that a mixture of coumarin-4-bromoacetic acid and 4-bromomethylcoumarins are produced when coumarin-4-acetic acids are brominated under certain definite conditions. The constitution assigned to these bromo derivatives was based on indirect though sufficiently clear evidence, but as the reactivity of the halogen in these compounds was very different from what might be expected of an alkyl bromide, it was considered expedient to obtain direct proofs, if possible, of the structure of these bromomethylcoumarins. It was believed that one of the best methods of settling the question would be to synthesise the same compounds from phenols and γ-bromoacetoacetic ester and our expectations in this direction have now been fully realised. The condensations of *m*-cresol and α-naphthol with γ-bromoacetoacetic ester have now been studied and the products shown to be identical with those prepared from 7-methylcoumarin-4-acetic acid and α-naphthapyrone-4-acetic acid respectively by bromination, thus setting at rest all doubts regarding the position of the bromine atom in these compounds. Moreover, the view that β-naphthapyrone-4 acetic acid proved to be an exception in furnishing not the expected β-naphthapyrone-4-bromacetic acid but the 3-bromo-β-naphthapyrone-4-acetic acid instead, has now been fully confirmed by synthesising the unknown 4-bromomethyl-β-naphthapyrone. The latter (m. p. 197°) is found to be quite different from the product of bromination of β-naphthapyrone-4-acetic acid after decarboxylation (m. p. 146°), and it is further converted by hot alkalis into the expected dihydrofuranonylacetic acid (m. p. 174°) and not the β-naphthafurancarboxylic acid (m. p. 242°) obtained by Dey and Radhabai (*loc. cit.*).

Experimental.

γ-Bromoacetoacetic ester was prepared by a slight modification of the method described by Conrad and Schmidt (*Ber.*, 1896, **29**, 1042).

From 18 g. of freshly distilled acetoacetic ester 11 g. of the pure γ-bromo derivative, b. p. 125°/10 mm. were obtained.

7-Methyl-4-bromomethylcoumarin.—A mixture of γ-bromoaceto-acetic ester (6 g.) and *m*-cresol (3 g.) was slowly added to ice-cold sulphuric acid (20 c.c.) with vigorous shaking and after standing in the ice-chest overnight, the deep red liquid was poured in a thin stream into 150 c.c. of ice water. A fine yellowish precipitate came down slowly; it was collected, washed with water and then with alcohol and the insoluble residue crystallised from boiling acetic acid as colourless shining plates, m. p. 236°, not depressed by admixture with the specimen obtained from the direct bromination of 7-methylcoumarin-4-acetic acid.

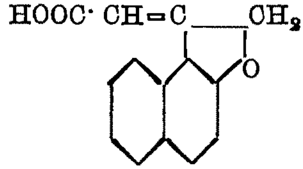
6-Methylbenzdihydrofuranonyl-3-acetic acid was obtained by the action of alkali on the bromo derivative. It crystallised from boiling water in long colourless needles, m. p. 107°, and was identified with the product prepared similarly from 7-methylcoumarin-4-acetic acid by bromination and subsequent alkali treatment (Dey and Radhabhai, *loc. cit.*).

4-Bromomethyl-α-naphthapyrone.—The thick yelow oil which separated on pouring the sulphuric acid solution of α-naphthol (4 g.) and the γ-bromoacetoacetic ester (6 g.) into water was converted into a granular yellow solid after repeated washing with alcohol. Two crystallisations from hot acetic acid gave bright yellow plates, m. p. 192°, yield 1 g. It was identified with the product of bromination of α-naphthapyrone-4-acetic acid by a mixed m. p. determination. (Found: C, 58·1; H, 3·34; Br, 27·1. $C_{14}H_9O_2Br$ requires C, 58·1; H. 3·11; Br, 27·7 per cent).

α-Naphthadihydrofuranonyl-3-acetic acid was obtained from the above by boiling with 2*N*-KOH for 20 minutes. It crystallised from boiling water in colourless needles, m. p. 162°. (Found: C, 73·9; H, 4·69. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·42 per cent).

4-Bromomethyl-β-naphthapyrone.—β-Naphthol (4 g.) and the bromoester (6 g.) were treated with sulphuric acid and the product worked up as before. It crystallised from acetic acid in golden yellow rectangular plates, m. p. 197°. (Found: C, 57·7; H, 3·39; Br, 27·1. $C_{14}H_9O_2Br$ requires C, 58·1; H, 3·11; Br, 27·7 per cent).

β-Naphthadihydrofuranonyl-3-acetic acid.



This was prepared by boiling the bromomethyl derivative with 2*N*-alkali for ½ hour. The acid crystallised from hot water in pale yellow needles, m. p. 172°. It decolourises bromine water and permanganate immediately in the cold. (Found: C, 74·1 ; H, 4·62. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·42 per cent).

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The Chemistry of Jute-lignin. Part IV. Dioxymethylene Group in Lignin.

By Pulin Behari Sarkar.

By the distillation of Willstätter-lignin Hägglund and co-workers (*Biochem. Z.*, 1924, **147**, 74; 1926, **179**, 376) obtained a product which could be condensed with phloroglucinol, barbituric acid, etc., but it was not furfural or any of its derivatives. Freudenberg and Harder (*Ber.*, 1927, **60**, 582) identified it as formaldehyde and considered it as a fission product of methylene dioxide group in lignin (*Ber.*, 1928, **61**, 1760). Fuchs and Horn (*Ber.*, 1929, **62**, 2647) got formaldehye but were unable to accept the hypothesis of Freudenberg because lignin gave comparatively more formaldehyde than its derivatives. Phillips and Goss (*J. Amer. Chem. Soc.*, 1932, **54**, 3374) obtained formaldehyde in some lignocelluloses but not in others and, therefore, regarded the presence of this group with uncertainty. In the present investigation, the problem has been studied with special reference to jute-lignin with a view to establish definitely the presence of this group in lignin (*cf. Cellulosechem.*, 1931, **12**, 263) and also to get an idea as to its molecular size from the amount of formaldehyde obtained assuming as Freudenberg does that only one such group is present in it.

In a series of papers from this laboratory it has been shown by Chowdhury and co-workers (*J. Indian Chem. Soc.*, 1929, **6**, 239; 1930; **7**, 347; 1932, **9**, 615) that ClO_2 is the mildest reagent known that separates lignin from cellulose and hemicelluloses without affecting the latter to any appreciable extent. But in the jute, thus delignified, the furfural value (as phloroglucide) was always found to be slightly less than the calculated figure, though lignin obtained therefrom gave no furfural after purification. This has recently been found to be the case with bamboo and cocoanut fibre as well (Chowdhury and Paul, unpublished paper). Jute, rice-straw, bamboo, cocoanut fibre and teak wood were distilled with 12% HCl and formadehyde was detected in all cases in the distillate with Schryver's reagent (*Proc. Roy. Soc.*, 1910, **B82**, 226). Lignin was

separated with 42% HCl in each case and formaldehyde could be found in every sample. As formaldehyde also gives an insoluble condensation product with phloroglucinol, the lower furfural values in delignified jute, bamboo and cocoanut fibre, etc., can now be properly explained. Delignified jute, bamboo, etc., give no formaldehyde on distillation with 12% HCl. As formaldehyde has also been found in chlorolignin obtained from jute directly or from separated lignin and purified by alcohol and acetone repeatedly, it cannot be regarded as an impurity as some workers in this field think. Freudenberg and Sohns (*Ber.*, 1933, **66**, 263) got it in lignosulphonic acid from pine-wood lignin and according to Kuster and Schoder (*Z. physiol. Chem.*, 1927, **170**, 44) a molecule of formaldehyde is supplied by lignin when heated with a little HCl and β-naphthol during the formation of merolignin.

Isolated lignin was distilled with 28% H_2SO_4 and formaldehyde was detected in the distillate as the white crystalline dimedone derivative (Weinberger, *Ind. Eng. Chem. Anal. Ed.*, 1931, **3**, 365) which was found to melt exactly at 187°. The distillate also developed fuchsine colour with Schryver's reagent which is characteristic of formaldehyde only.

From HCl-lignin on distillation with 28% H_2SO_4 or 20% NaOH a distillate was obtained which gave iodoform with iodine and alkali. Hence the well known iodometric method could not be employed for the estimation of formaldehyde. As iodoform was still obtained when formaldehyde was removed by dimedone which reacts with aldehydes only, and as the distillate gave no aldehyde on oxidation with potassium dichromate and sulphuric acid, most probably it is a ketone. As a matter of fact, higher results were obtained by the potassium cyanide method than by the dimedone process. Thus, the latter appears to be the only accurate and reliable method which has been employed here all along for the estimation of formaldehyde. This method compares favourably with the other two as has been found with a known dilute solution of formaldehyde. 28% Sulphuric acid has been found to be the best hydrolysing agent. Obviously the method fails if lignin gives furfuraldehyde on acid distillation. In a former paper (*J. Indian Chem. Soc.*, 1931, **8**, 397) it was shown by the author that HCl-lignin from jute after proper purificaton gave no furfural. Lignin was then boiled with 3-4% acid for 1 to 2 hours during isolation. It has now been observed that much of the dioxymethylene group is lost thereby. It has been possible to free HCl-lignin from pentosans by first of all washing the former free from acid and then boiling with

water until the filtrate no longer reduces Fehling's solution. The lignin thus obtained gave much more formaldehyde.

The highest yield of formaldehyde recorded by Freudenberg and co workers (*Ber.*, 1933, **66**, 262) from pine-wood lignin was 1·2% only. Depending partly on this result they advanced a structural formula for lignin corresponding to a mol. wt. of 2140 (in unpolymerised form). But as the mol. wt. of lignin derivatives, so far determined by different workers, lie between 800 and 1000 (Fuchs, "Chemie des Lignins," 1926, p. 178) it is difficult to reconcile Freudenberg's figure with these. The dioxymethylene group has been found to be very unstable towards acids. Thus, when lignin was prepared by 72% sulphuric acid and boiled with 3-4% acid during isolation, the % of formaldehyde was 0·21 only. It was higher (0·65%) by the 42% HCl method followed by dilute acid boiling. When the latter step was omitted and lignin was separated by 42% HCl at 29° the % rose higher, *viz.*, 0·247%, and when lignin was separated at 20° for 24 hours 2·13% was the yield of formaldehyde. It was a very light powder of pale brown colour, while deep grey or almost black variety was obtained at higher temperature and prolonged exposure. Lastly this sample was washed repeatedly with dilute caustic soda until the washings were colourless, the maximum amount was obtained (2·63%). The % of formaldehyde fell down considerably if the lignin was exposed to the action of fuming hydrochloric acid for too long a time, the temperature remaining constant.

But this figure, too, does not represent the total amount of formaldehyde, as from piperonylic acid theoretical yield of it is never obtained. Freudenberg (*Ber.*, 1927, **60**, 581) explained it by saying that as soon as the formaldehyde was split off it combined with the protocatechuic acid thus formed to give back the original compound, as he got only 71% of formaldehyde. This explanation does not appear to be sound for the simple reason that according to the law of mass action, when one of the resultants (H·CHO) is free to leave the sphere of action, the reaction is bound to go to completion. Moreover, it is most unlikely that in a hydrolysing medium the methylenedioxide group should be re-introduced, a process accompanied by elimination of a molecule of water. Again, by following the method of Clowes (*Ber.*, 1899, **32**, 2842) in which the split off formaldehyde forms an insoluble compound with phloroglucinol *in situ*, far higher results were obtained for H·CHO, though both piperonylic and protocatechuic acids are fairly soluble in hot

water. It is a well known fact that phenol and formaldehyde combine at about 150° to give a resin, 30% H_2SO_4 or dilute hydrochloric acid being used as catalysts. (Bary and others, "Natural and Synthetic Resins," p. 118). Far less than the actual amount of H·CHO was obtained when a known quantity of a dilute solution of H CHO was distilled with vanilic acid, and absolutely nil with phenol; with protocatechuic acid only 77·61% of HCHO was obtainable. It is important to note here also that in the aliphatic series cent per cent HCHO was obtained by Clowes (*loc. cit.*) The phenolic groups set free, therefore, appear to be responsible for the lower yield of formaldehyde and resin formation is the most probable explanation. It has been found that no carbon separates when piperonylic acid is distilled with acid, as the residue dissolves in caustic soda to a clear solution. Hence the lower yield of HCHO cannot be thus accounted for. After solubility correction, the figure for HCHO stands at 2·78 % and assuming that this represents only 77·6% of theory, and also that only one $O{\cdot}CH_2{\cdot}O$ group is present in lignin, its mol. wt. comes to 830, which is in fair agreement with those otherwise obtained. Rassow and Wagner (*Cellulosechem.*, 1932, **13**, 109) determined the mol. wt. of glycol-lignin by Barger-Rast method and gave the figure as 840.

Lignins from various sources have almost without exception been found to reduce Fehling's solution. Friese (*Ber.*, 1929, **62**, 2538) considered it to be due to the presence of traces of sugars, while according to Powell and Whittaker (*J. Chem. Soc.*, 1925, **127**, 132) the lignin molecule contained one active aldehyde group (*cf.* Heuser, *Paper Trade J.*, 1930, **88**, 75; Klason, *Ber.*, 1932 **65**, 625). The dioxymethylene group present in lignin suffers decomposition to a greater or less extent during isolation, depending on the method employed. The two phenolic groups in the *ortho*-position, which thus result, have now been found responsible for the reducing action. It has thus been possible to separate lignin obtained by 42% HCl at 20° for 24 hours into two fractions by repeated treatment with dilute caustic soda at room temperature in a glass filter, until the washings are colourless. The soluble fraction reduced Fehling's solution and liberated silver from an ammoniacal solution of silver nitrate, just like protocatechuic acid or pyrocatechol, while the insoluble one (major portion) showed no reducing property at all. The percentage of HCHO in this rose up to 2·68%. Moreover, when all the HCHO was distilled off from the insoluble

fraction, the residue left was soluble in NaOH and again reduced Fehling's solution. The higher the temperature, and the longer the time of exposure to the acid, the less has been found the percentage of HCHO in the separated lignin and the stronger the reducing action as well.

In order to prove more directly that the HCHO in lignin comes from the $O \cdot CH_2 \cdot O$ group present in it, all the HCHO was distilled off from lignin with 28% H_2SO_4 and the residual substance was treated in a sealed tube at 140-50° with methylene iodide and caustic potash in absence of moisture, according to the method of Fittig and Remsen (*Annalen*, 1873, **168**, 94). The purified product, completely freed from CH_2I_2, again gave HCHO on distillation with acid. The process of methylenation was repeated thrice and the final product after alkali-washing was found to give practically the same amount of HCHO (2·81%) as the original lignin and it no longer reduced Fehling's solution. The $O \cdot CH_2 \cdot O$ group has been found to be more or less unaffected during halogenation and treatment with boiling alcoholic potash. On distillation with 20% NaOH no trace of HCHO could be split off from lignin. The observations of Freudenberg and Sohns (*Ber.*, 1933, **66**, 262) that the $O \cdot CH_2 \cdot O$ group is decomposed by dilute alkali, could not, therefore, be confirmed in the case of jute-lignin.

In view of the fact that higher yield of HCHO was obtained from lignin separated at low temperature, an attempt was made to isolate the same at very low temperature with 42% HCl but unfortunately it was found that below 20° no complete separation was possible ; a rose coloured cellu-dextrine type of substance was obtained, which gave a white powder by the action of ClO_2 in aqueous suspension. With 72% H_2SO_4 as well the same difficulty arose and even the lignin obtained at 20° had a far lower HCHO value.

So long the methoxy content used to serve as the only criterion for the purity of lignin, the higher the value the purer was considered the product. But this is quite defective as by NaOH under pressure (Mehta, *Biochem. J.*, 1925, **19**, 958) a lignin was obtained from jute which had 20·1% methoxy value (Sarkar, *J. Indian Chem. Soc.*, 1931, **8**, 401) although it was fairly soluble in water. As the mildest procedure has to be adopted in obtaining a lignin with high % of HCHO, obviously the methoxy groups remain unaffected. As a matter of fact, 16·41% methoxy has been

found in such a sample. The $O \cdot CH_2 \cdot O$ group rather than the methoxy alone should, therefore, be regarded as the criterion. It is thus becoming increasingly difficult to lend support to the theory that pectin or hemicelluloses are the precursor of lignin. As will be shown later on, the acetyl group also is characteristic of pectin and not present in lignin.

It is interesting to note in this connection that traces of HCHO have been obtained by the author from glucose and fructose on distillation with 28% H_2SO_4 or 12% HCl. But there is no plausible ground to draw the conclusion that these sugar residues are present in lignin; because they always gave furfural or its derivative under such conditions, while lignin gave none, and secondly the amount of HCHO was extremely small being present only in the first 10-15 c.c. of the distillate and could only be detected by Schryver's reagent, while lignin (0·3-0·4 g) took about 4-5 hours to part with its formaldehyde.

Experimental.

In order to show that the percentage of furfural in delignified lignocelluloses is always lower than the calculated amount, furfural was carefully determined by the phloroglucide method of Tollens and Bodner (*Z. Landwirt*, 1910, **68**, 232) by distillation with 12 % HCl. The precipitation was done in the cold as Klingstedt (*Z. anal. Chem.*, 1925, **66**, 129) has shown that better results are thus obtained. The figures calculated on dry sample are shown below.

TABLE I.

Substance.	Lignin (HCl-method).	Furfural (on raw sample).	Furfural (in delignified sample).	Furfural (calculated on raw sample).	Deficiency.
Jute	15·43%	9·54%	8·86%	7·50%	13·22%
Bamboo	27·50	14·50	14·30	10·36	15·05
Cocoanut fibre	49·50	13·58	12·50	6·31	14·58

On distillation with 12% HCl raw straw, bamboo, jute, etc., gave both furfural and formaldehyde and the former was tested as

usual with aniline acetate paper which remained unchanged by formaldehyde and the latter by Schryver's reagent after much dilution. In very dilute solution, furfural does not interfere with the test for formaldehyde.

In the estimation of formaldehyde by the dimedone method, about 0·5 g. of dry and finely powdered lignin, purified from furfural-yielding substances, was distilled at 140-50° with 100 c.c. of 28% H_2SO_4 according to Tollens' method; 30 c.c. of distillate were collected and 30 c.c. of boiling water added to maintain the same strength of the acid. It was necessary to add a little powdered charcoal (Merck's reagent) to prevent frothing and consequent overflowing in some cases. The distillation was continued until the test for HCHO was negative. 20 C.c. of 2% dimedone in dilute NaOH were added and the liquid made just acid with acetic acid. The flask was kept at 4° for 24 hours in a frigidier after addition of 200-250 c.c. of a saturated solution of NaCl to reduce the solubility of the derivative. The precipitate was filtered in a glass filter under very mild suction and washed free from chloride It was dried at 110° and weighed. In one sample 0·2825 g. of lignin gave 0·0724 g. of the derivative, whence HCHO=2·63% (without solubility correction). The shining crystals are extremely soluble in acetone, alcohol and benzene. Weinberger has shown that the solubility of the derivative is 0·0005g. per 100 c.c. at 19°. A similar correction has been introduced in this case also.

To see how this method compares with the ordinary ones, a very dilute solution of HCHO (about 3·20 g. per litre) was used for the estimation by all these methods. It may be pointed out here that in the iodine method, the time should be at least half an hour and not 10 minutes as Treadwell (1924, Vol. II. p. 589) says. In the cyanide method, only a few drops of the saturated solution of ferric alum should be added and not 5 c.c. as recommended by the "Official and Tentative Methods of Analysis" (U. S. A., 1925, p. 68), otherwise anomalous results are obtained in the case of dilute solution. In order to see if a portion of the HCHO is lost during distillation, 10 c.c. of the HCHO solution were distilled with 28% H_2SO_4 (100 c.c.) as in the dimedone method and HCHO was estimated in the distillate. The following table will show that concordant results are obtained in either case. The figures for HCHO from HCl-lignin are also given below.

TABLE II.

10 C.c. of HCHO soln. taken.	Cyanide method.	Iodine method.	Dimedone method.
Without distillation	31·85 mg.	30·96 mg.	30·66 mg
After "	31·08	30·84	30·71
From HCl-lignin	2·31%	2·60%	1·45%

The influence of the strength of H_2SO_4 on the yield of HCHO was next studied with the same sample of lignin and H_2SO_4 of different strength by employing the dimedone method. The following table will show that 28% H_2SO_4 is the best for the purpose. HCl-lignin separated at 29° for 24 hours without acid boiling.

TABLE III.

H_2SO_4 conc. (%) ...	15·71	22·19	28·22	34·57	40·35
HCHO obtained (%)	0 59	0·81	0·947	0·78	0·324

Formaldehyde was estimated in different samples of lignin isolated under different conditions. The results are shown below.

TABLE IV.

Methods of isolation.	HCHO found.
(1) 72% H_2SO_4 at 29°, for 36 hrs. acid boiling	0·21%
(2) " " " without acid boiling	0·38
(3) Moistened with HCl, then 72% H_2SO_4 for 24 hrs.	0·42
(4) 42% HCl at 29°, 36 hrs. acid boiling	0·652
(5) " " without acid boiling	0·947
(6) " at 20° for 24 hrs. "	2·63
(7) " at 4° for 10 hrs. and at 28° for 12 hrs.	1·82
(8) Sample (6) with 42% HCl at 20° for 24 hrs	2·02
(9) Sample (7) boiled with 4% alc. KOH for 4 hrs.	1·76
(10) 72% H_2SO_4 at 4° for 10 hrs. and at 30° for 13 hrs.	0·53

The effect of the presence of phenolic bodies on the yield of HCHO was then studied by distilling 10 c.c. of the HCHO solution

with phenol, vanillic acid, etc. Table V shows the yield in the distillate. 28% H_2SO_4 was used at a temperature of 140-60° as usual.

TABLE V.

10 C.c. of HOHO distilled with	HOHO recovered	Yield.
(a) Alone	30·97 mg.	100%
(b) Phenol (1 g.)	Nil	Nil
(c) Vanillic acid (1·5 g.)	2·00	6·45
(d) Protocatechuic acid (1·5 g.)	24·04	77·61

Molecular weight of lignin.—As mentioned above the highest yield of formaldehyde is 2·63%, making a correction for the solubility it comes 2·778%. Assuming this is only 77 , the theoretical yield amounts to 3·61%. Further, on the assumption that only one $O \cdot CH_2 \cdot O$ group is present in the molecule, 30 g. of HCHO are to be obtained from 830 g. of lignin, which figure therefore stands for its molecular weight.

Methylenation of lignin.—About 1 g. of lignin (HCHO, 2·63%), from which all HCHO was distilled off, was dissolved in a concentrated solution of KOH (5 g. in 10 c.c.) and dried at 105°. The finely powdered substance was mixed with 5 c.c. of methylene iodide (16 g.) and heated in a sealed tube in glycerine-bath at 140-50° for 7-8 hours. The light brown mass was washed with ether to remove the excess of methylene iodide and then with water until neutral. Lastly it was boiled with water and steam was passed through it to expel the last trace of methylene iodide. It was then dried and HCHO was estimated in the sample. The product was of light brown colour. The process is far from being quantitative only a small yield of methylenated product being obtained by a single treatment. The results are shown below.

TABLE VI.

Sample treated.	No. of treatment.	HCHO.
HCl-lignin after distilling off the HCHO	1	0·91%
	2	1·34
	3	1·84
		2·31
H_2SO_4-lignin with 0·38% HCHO	1	1·003

6

SUMMARY.

1. The lower yield of furfural in delignified jute, etc., is due to $O{\cdot}CH_2{\cdot}O$ group in lignin, and lowering of percentage is nearly the same in three samples analysed.

2. Five lignocelluloses have been found to give formaldehyde as also lignins obtained therefrom, $O\text{-}CH_2\text{-}O$ group thus appears to be a common constituent of lignin.

3. Dimedone method is the only one applicable in the case of lignin, this gives identical results with that by iodine or cyanide method in dilute solution.

4. 28% H_2SO_4 gives the best result for HCHO, stronger or weaker acids giving lower values.

5. Prolonged exposure to strong acids, higher temperature and subsequent acid boiling considerably lower the yield of HCHO in lignin. Best results have been obtained at 20° for 24 hours, acid boiling being omitted.

6. Lower yield of HCHO from lignin is due to resin formation with phenolic bodies and not to the re-formation of the original substance.

7. The reducing action of lignin is due to two OH groups in the *ortho*-position set free during isolation and not to any CHO group.

8. The presence of $O{\cdot}CH_2{\cdot}O$ group has been established by methylenation.

9. The mol. wt. of lignin has been calculated as 830 from the yield of HCHO, which is in close agreement with figures otherwise obtained.

My grateful thanks are due to my Professor Dr. J. K. Chowdhury for the kind interest he has all along taken in the work and to Prof. J. C. Ghosh for giving me every facility to carry it out. My thanks are also due to Prof. S. N. Bose for kindly helping me with discussions and criticisms.

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Magnetic Study of Mixed Crystals of Sytem S—Se.

By S. S. Bhatnagar and Pyara Lal Kapur.

The magnetic properties of binary systems with metallic components which either form continuous solid solutions or are partially miscible, have already been studied by various workers (*cf.* Honda and Sone, *Sci. Rep. Tohuku Imp. Univ.*, 1913, **2**, 1; Endo, *ibid.*, 1925, **14**, 479; Garrison, *J. Amer. Chem. Soc.*, 1925, **47**, 622; Spencer and John, *Proc. Roy. Soc.*, 1927, **A 116**, 61), and that of binary system of salts has been studied by the present authors (*J. Indian Chem. Soc.*, 1932, **9**, 347). So far as the authors are aware a binary system with non-metallic components has not been studied from this point of view, therefore the study of the magnetic property of S—Se system, a non-metallic one, forms the subject of the present investigation.

From phase-diagram point of view the system has been studied by Rathke (*Annalen*, 1869, **152**, 188) and later on by Rath and Bettendes (*Pogg. Ann.*, 1879, **139**, 329); but it was thoroughly investigated by Ringer (*Z. anorg. Chem.*, 1902, **32**, 183). He found that melted Se and liquid sulphur can be mixed in all proportions, but it is very difficult to crystallise it out when Se content is more than 10%. In the present investigation, therefore, the magnetic property of mixed crystals, whose Se content does not exceed 10%, has only been studied.

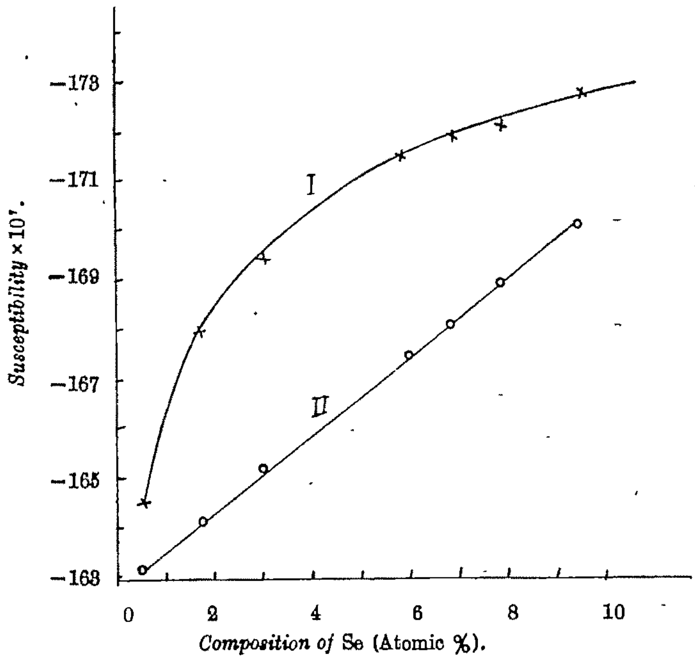
Experimental.

Sulphur, from which the mixed crystals were prepared was the purest obtainable and further purified by crystallisation from pure carbon disulphide. Selenium was available in the form which was insoluble in CS_2 ; therefore the soluble form was prepared by dissolving the available variety in HNO_3 and HCl and by reducing the selenious acid thus formed to red amorphous Se by SO_2. Se thus formed was filtered, washed thoroughly with alcohol and was dried in an electric oven maintained at 40°. Before use the purity of the

elements was further tested by determining their melting points and specific gravities which are given in Table I and for comparison the values given in books are added in parenthesis.

FIG. 1.

S—Se *System.*



I—Susceptibility of mixed crystals.
II—Susceptibility of mixture.

TABLE I.

Substance.	M. p.	Sp. gr.
Rhombic sulphur	113° (115°)	2·04 (2·037)
Red selenium	215° (212-217°)	4·39 (4·36)

The thermal method of preparing the mixed crystals was not resorted to in order to avoid any complication that may arise on account of chemical transformation, such as oxide formation and the appearance of the phenomenon of allotropic modification at high temperatures, but the mixed crystals of S—Se were prepared by precipitation from CS_2 solution. Saturated solutions, both of S and

Se, were prepared in hot CS_2 and were mixed in different proportions. The solvent was allowed to evaporate gradually and the crystals that separated were quickly filtered off and dried with filter paper. These crystals were placed in an oven maintained at 40-45° for a number of hours in order to get rid of any CS_2 that might be sticking to the crystals, and after that the crystals were placed in a vacuum desiccater till further use. The crystals thus obtained were all rhombic resembling the sulphur crystals but their colour varied from dark-red to brown-red. The samples got in this way were analysed for Se and S, both by dissolving them in HNO_3 and a small quantity of bromine. Sulphur was estimated from the solution by the usual SO_4 method and Se by reducing selenious acid thus formed by hydroxylamine hydrochloride to red amorphous Se.

Data for the densities of the samples as determined are given in Fig. 1, and in Table II.

TABLE II.

Density of the mixed crystals.

(Se) % ...	0	1·19	4·10	7·25	13·86	15·57	17·42	20·71	100
Density (obs.)	2·04	2·09	2·18	2·25	2·40	2·455	2·51	2·58	4·39
Density (calc.)		2·06	2·13	2·21	2·35	2·405	2·449	2·52	—

The magnetic susceptibility of mixed crystals was determined by the magnetic balance of the Wilson type which was used in our previous work.

Pure water which has a mass susceptibility of $-7{\cdot}2\times10^{-7}$ was used as the comparison substance in all determinations.

Susceptibility of the pure components.—The mass and the atomic susceptibility of the pure element, from which the mixed crystals were obtained are given in Table III and for comparison values obtained by others workers are added.

TABLE III.

Element.	Observed. $\chi\times10^7$.	Observed. $\chi_{at}\times10^7$.	Other workers. $\chi\times10^7$	Other workers. $\chi_{at}\times10^7$.
Rhombic sulphur	−5·08	−162·9	−5·1 (Curie) −4·9 (Pascal)	−160·0 (Bhatnagar and Dhawan)
Selenium	−3·04	−240·7	−3·04 (Honda and Sone) −3·1 (Curie)	−235·0 (Pascal) −254·0 (Bhatnagar and Dhawan)

The values of susceptibility with composition of the mixed crystals and of mechanical mixture are tabulated in Table IV and the curve plotted is given in Fig. 1.

TABLE IV.

	Wt %	Atom % Se.	$\chi \times 10^7$ Mixed crystals.	Atomic wt.	$\chi_{a} - 10^7$ Mixed crystals.	Mechanical mixture.
A.	1·19	0·48	−5·09	32·32	−164·5	−163·1
B.	4·10	1·70	−5·11	32·86	−167·9	−164·1
C.	7·25	3·06	−5·06	33·50	−169·5	−165·2
D.	13·36	5·88	−4·92	34·85	−171·5	−167·6
E.	15·57	6·90	−4·87	35·31	−171·8	−168·1
F.	17·42	7·86	−4·81	35·76	−172·0	−168·8
G.	20·71	9·50	−4·74	36·52	−172·8	−170·0

DISCUSSION.

In discussing the results the following factors have to be taken into consideration.

(*a*) *Effect of impurities.*—Spencer and John (*loc. cit.*) observed that magnetic susceptibility of alloys of elements particularly of Pb and Hg, which form mere mechanical mixtures of Pb and Hg in all proportions, did not show a linear relation between susceptibility and concentration as it should have; but on the other hand so marked were the deviations that alloys containing 3·6% to 47·6% by weight of lead were found to be strongly paramagnetic notwithstanding the fact that both pure lead and silver are diamagnetic. Montgomery and Ross (*Phys. Rev.*, 1933, **43**, 358) have, however, very recently observed that magnetic susceptibility of lead and silver alloys does vary linearly with composition and suggest that the departures from linear relation observed by Spencer and John (*loc. cit.*) are on account of iron contamination.

In the present investigation, therefore, special precautions were taken to ensure the purity of the components as well as of the mixed crystals. Various physical properties, such as density, melting point, and magnetic susceptibility of the elements were determined

before use and the specimens having values corresponding to those given in standard books were only used. CS_2 could be the only possible impurity in the mixed crystals. This impurity was kept out by maintaining the oven at 40-45° temperature which is the boiling point of CS_2. They were further placed in a vacuum desiccator.

(b) *Effect of absorbed gasses.*—Shimizu (*Sci. Rep. Tohuku Imp. Univ.*, 1932, **21**, 826) has recently shown that in most cases the rapid decrease of magnetic susceptibility of an element like Bi, or Sb on the addition of an element like Sn, Te or Pb was not due to the formation of solid solution between the two elements, as was previously supposed, but was due to the absorbed gases in alloys. Alloys are generally prepared by heating the components to high temperature and then allowing the mass to cool. It is during this process of cooling that various gases are absorbed. In this system of S—Se the possibility of gases being absorbed is remote because the mixed crystals have been prepared at ordinary temperatures out of solution and not at high temperatures employed in the preparation of the alloys.

Moreover, if the gases had been absorbed then the value of the susceptibility would have decreased but on the other hand we find that the values had actually increased. From the table it is clear that if the concentration-susceptibility graph be plotted, then the curve will not follow the linear path which it would have were it to obey the simple additive law of Pascal for mixtures, but it follows a curved path. The maximum deviation from the additive value has been found to occur at a point where S and Se exist in a ratio 32:1. It is well known that both S and Se exist in various molecular complexes as S_8, Se_8, Se_{16}, Se_{32}.

The crystal pattern of sulphur consists of 128 atoms of sulphur. The deviation from the additive law, therefore, would appear to be due to the formation of S—Se complexes which may be represented by the general formula $S_x\ Se_y$ where x and y are any numbers.

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Action of Amines on Quinolinic Acid.

By Ananda Kishore Das and Indu Bhuson Sarker

The action of mono- and diamines on phthalic acid has been studied by several investigators. A study of similar reactions on quinolinic acid was expected to be of interest.

Ghosh (*J. Chem. Soc.*, 1919, **115**, 1105) in an attempt to prepare compounds like phthaleins from quinolinic acid noticed that with aniline it gave quinanils similar to phthalanils. Sen-Gupta and Sarkar (*J. Indian Chem. Soc.*, 1928, **5**, 401) studied the action of benzidine and tolidine on it, while Sircar (*J. Indian Chem. Soc.*, 1932, **9**, 145) also studied in detail the action of phenylhydrazine.

Philips (*Ber.*, 1894, **27**, 839) studied the action of ammonia on quinolinic acid. It was thought desirable to follow the course of the reaction of this compound with mono- and diamines. In this paper, its action on aniline has been studied under different experimental conditions.

When aniline is mixed with quinolinic acid the mixture gets warm and aniline quinolinate (mono) is formed, a possibility forshadowed by Meyer (*Ber.*, 1899, **32**, 2122). On keeping this compound just near its melting point for a few minutes it changes to diquinolinate. Either of the above or a mixture of aniline and quinolinic acid on heating with glacial acetic acid gives the dianilide which when heated at225-240° changes to quinanil (Ghosh, *loc. cit.*, records m.p. 248-251° ; Engler, *Ber.*, 1894, **27**, 1789, gives 228°). The quinanil on boiling with alcoholic ammonia changes to quinanilic acid, m. p. 217° and this changes back to the anil on heating.

The fact that the quinolinates respond to diazo test and regenerate aniline on treatment with cold dilute caustic soda proves that they are additive compounds, which is also confirmed by analysis.

The quinanil obtained by Engler, Ghosh and by the present authors differs widely in its melting point, and while the compound obtained by Ghosh's method could not be hydrolysed by boiling

alcoholic-potash or strong hydrochloric acid, that obtained by us could easily be hydrolysed by either of these reagents.

A study of literature of the corresponding compounds of phthalic acid reveals a similar divergence in the melting points. Thus phthalanilic acid has been found to have a melting point of 158° (Zincke, *Annalen*, 1884, **225**, 375), 170° (Meyer, *loc. cit.*), 192° (Laurent, *J. Chem. Soc.*, 1847, **48**, 605). Phthalyldianilide has m p. of 251° (Meulen, *Rec. trav. chim.*, 1897, **16**, 346) and 231° (Rogoff, *Ber.*, 1897, **30**, 1442).

An attempt was, therefore, made to isolate some of these compounds to get a clue to this peculiar divergence in their melting points. It has been found that while Meyer's compound is the real phthalanilic acid, that of Zincke is a phthalate with one molecule of aniline, the additive nature of the compound is determind as with the corresponding compounds of quinolinic acid.

Experimental.

Aniline quinolinate (mono).—Quinolinic acid (0·5 g.) and excess of aniline when mixed in a test tube got warm and soon changed to a solid mass. After leaving overnight, the solid was crystallised from alcohol as colourless prisms, m. p. 187° (decomp.). It solidifies at about 160-65° and remelts at 187°. It is highly soluble in alcohol and acetic acid. It also dissolves readily in a solution of sodium carbonate with effervescence and in cold caustic soda with separation of aniline. It responds to diazo test. (Found: N, 11·1 ; aniline, 36·1. $C_{13}H_{12}N_2O_4$ requires N, 10·8 ; aniline, 35·8 per cent).

Aniline quinolinate (di-)—The above substance (0·5 g.) was heated in a test tube gradually up to its melting point and the temperature raised slowly up to about 160°. The solid is crystallised from alcohol as colourless needles, m. p. 187° (decomp.). It is soluble in alcohol and acetic acid and also dissolves in caustic alkalis in the cold with separation of aniline. It can be diazotised with cold dilute HCl and coupled with β-naphthol. (Found: aniline, 52·0. $C_{19}H_{19}N_3O_4$ requires aniline, 52·0 per cent).

Quinolinyl dianilide.—A mixture of quinolinic acid (1 part) and aniline (2 parts) and a few drops of glacial acetic acid was heated on a water-bath for abont 3 hours. The mixture at first melted and then solidified. The solid was collected and crystallised from alcohol in long colourless needles melting at 225°. It is soluble in boiling

alcohol and insoluble in cold alkalis and can be hydrolysed with strong hydrochloric acid. (Found: N, 13·5; aniline, 59·0. $C_{19}H_{15}N_3O_2$ requires N, 13·25; aniline, 58·7 per cent).

(*a*) Quinolinic acid (0·5 g.) was mixed with excess of acetanilide and heated at 125° for 2 hours. On cooling the solid was crystallised from alcohol as fine colourless needles, m. p. 225°.

(*b*) Aniline quinolinate (mono) was heated above 187° for 3 hours. When frothing was over the product was crystallised from alcohol as colourless needles, m. p. 225°.

(*c*) Aniline quinolinate (di-) was kept above its melting point for about an hour. The solid when crystallised melted at 225°.

Quinanil.—Quinolinyl dianilide (0·5 g.) was heated at 225-240° for 1 hour and the solid crystallised from alcohol in colourless needles, m. p. 208°. It is soluble in alcohol and acetic acid but insoluble in cold caustic soda. (Found: N, 12·8; aniline, 40·8. $C_{13}H_8N_2O_2$ requires N, 12·5; aniline, 41·5 per cent).

Quinanilic acid.—Quinanil (0·5 g.) was heated with alcoholic ammonia for an hour under reflux. The solid separating was filtered, acidified with acetic acid, washed and crystallised from hot alcohol in colourless laminæ, m. p. 217° (decomp.). It is soluble in alcohol and in sodium carbonate solution with effervescence. If kept at the temperature of decomposition for about 15 minutes it changes to quinanil melting at 208°. (Found: N, 12·2; aniline, 39·0. $C_{13}H_{10}$-N_2O_3 requires N, 11·5; aniline, 38·4 per cent).

Aniline phthalate (mono).—Phthalic acid (1 g.) was mixed with excess of aniline. The mixture which got warm and soon solidified was left overnight. The solid was crystallised from alcohol in colourless needles, m. p. 158° (decomp). It is soluble in alcohol and acetic acid and dissolves in cold sodium carbonate soluton with the separation of aniline. It responds to diazo test (Found: aniline, 35·9. $C_{14}H_{13}O_4N$ requires aniline, 36·0 per cent).

Phthalic acid (1 g.) and excess of aniline was heated in a toluene bath for 1 hour. The solid that separated on cooling crystallised from alcohol in needles, m. p. 158°.

Phthalanil.—The above substance was kept at a temperature of 160-65° for an hour and the solid crystallised from alcohol in colourless needles, m. p. 205°. (Laurent gives the m. p. 203-05°).

Phthalanilic acid.—Phthalanil (1 g.) was heated with alcoholic potash for 15 minutes. The solid that separated on cooling was washed with dilute acetic acid and then crystallised from alcohol in

colourless needles, m. p. 170°. (Meyer, 170°; Zincke, 158°; Laurent, 190°).

This substance cannot be diazotised with cold dilute hydrochloric acid as the one melting at 158°, but can be diazotised after boiling with strong hydrochloric acid. When heated above its m. p. it is converted readily into phthalanil.

The percentage of nitrogen in anils, anilides and quinolinates being very close it was thought desirable to confirm the results by estimating volumetrically the aniline content, where the divergence of percentage is greater, in the different types of compounds by the Maurice Franchois method (*J. Phar.*, 1899, *vi*, 9, 521) which was found to work very statisfactorily.

Further work is in progress. We take this opportunity of thanking the Principal of the college for his kind interest in the work.

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Actinodaphne Fat as a Parent Material for a New Detergent. A Note.

By S. V. Puntambekar and S. Krishna.

In our paper on the fat and oil from the seeds of *Actinodaphne hookeri*, Meissn (*J. Indian Chem. Soc.*, 1933, **10**, 395) it was pointed out that the fat could be employed as a source of lauric acid. Recent work on new detergents (Duncan, *Ind. Eng. Chem.*, 1934, **26**, 24) has shown that the alkali salts of lauryl sulphate possess certain properties which from the point of view as detergents are superior to those possessed by the ordinary soap. For instance, the amount of sodium lauryl sulphate required for washing is practically independent of the hardness of water, whereas the amount of the ordinary soap required to do the same work increases rapidly with the hardness. This is because its calcium and magnesium salts, unlike the calcium and magnesium salts of the fatty acids of high molecular weight, are themselves good sudsents and good detergents. Furthermore, sodium lauryl sulphate is not easily affected by salt as the ordinary soaps are and performs as well in sea water as in tap water. The solubility and the sudsing capacity of sodium lauryl sulphate is more affected by temperature than that of the soap of corresponding molecular weight. It is, however, sufficiently soluble to sud, well in ice-cold water.

Sodium lauryl sulphate is being sold in the U. S. A. as 'Gardinol W. A.' in the textile trade and as 'Orvus' in other bulk supplies; and these developments in the field of soap chemistry have met with considerable trade acceptance. It has further found use as 'spirit cleaner' in which case a small amount of the sodium lauryl sulphate is dissolved in hydroalcoholic mixture containing about 35% alcohol and 5% glycerine.

For the preparation of the sodium lauryl sulphate, lauryl alcohol has hitherto been obtained by hydrogenation of either the cocoanut or the palm kernel oil followed by fractional distillation. The kernel fat of *Actinodaphne hookeri* which contains 96% of trilaurin can, we suggest, be used more suitably for the purpose and in this note we, therefore, record the preparation and yields of trilaurin, methyl laurate and lauryl alcohol compounds which have now acquired considerable commercial significance.

Experimental.

Trilaurin.—1 Kilo. of the kernels of *Actinodaphne hookeri* seeds was crushed and expressed at about 40° in a hydraulic press, yielding 480 g. (48%) of a pale yellow oil which on cooling became hard and crystalline. The residual cake on being extracted with petroleum ether further gave 270 g. of the oil, making a total yield of 750 g. (75%).

200 G. of the fat were dissolved in 2 litres of 95% hot alcohol and the contents of the flask shaken during cooling, thus preventing the separation of trilaurin as an oily product. Trilaurin crystallised out in snow-white needles which on removal and drying weighed 170-180 g. (85-90% yield).

Methyl laurate.—In 200 g. of the fat in 2 litres of methyl alcohol dry hydrogen chloride was passed upto 3%, after which the alcohol was distilled off. The residual esters were washed with sodium carbonate (2·5%) and then with water and the dried esters were submitted to fractional distillation at 5 mm. The fraction boiling at 127-130°, is methyl laurate which is obtained in a yield of 90-95% (173-182 g.).

Lauryl alcohol was obtained by the modified method of Ford and Marvel ("Organic Syntheses," Vol. X, p. 62) the yield being 65-75% of the theoretical amount.

Sodium lauryl sulphate could be prepared by treating the lauryl alcohol with concentrated sulphuric acid in presence of acetic anhydride with or without a catalyst (*Deuts. Hydrierwerke* A.-G., B. P. 307, 709 ; H. T. Böhme A.-G., B. P. 317,089).

For commercial purposes the alcohol could easily be obtained by the high pressure hydrogenation (Schrauth, Schenck and Stickdorn, *Ber.*, 1931, **64B**, 1814) of trilaurin from *Actinodaphne* fat and from the similarly constituted fats *Litsaea* species (N. O. Laurinaceae) over sixty varieties of which are known to be found all over the country and which could serve as an easy and a cheap source of the raw material. *Litsaea sebifera* fat, for instance, contains 96% trilaurin (Schroeder, *Arch. Pharm.*, 1905, **243**, 631) and *Litsaea zeylanica* contains 85% (unpublished results by the authors). The fats from other Indian *Litsaeas* are under investigation.

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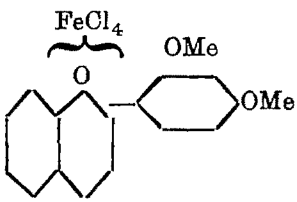
Synthesis of Benzopyrylium Compounds. Part I.

By M. Goswami and A. Chakravarty.

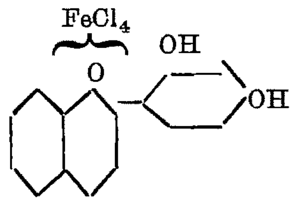
It has been established by the authors (*J. Indian Chem. Soc.*, 1932, 9, 599) in a preliminary note on the subject that coumarins condense with phenols to give benzopyrylium compounds when phosphorus oxychloride is used as condensing agent. The following compounds prepared by the new method have already been described:

(I) 2′:4′-Dimethoxy-2-phenylbenzopyrylium ferric chloride (from coumarin and dimethoxyresorcin).

(II) 2′:4′-Dihydroxy-2-phenylbenzopyrylium ferric chloride (from resorcin and coumarin).



(I)



(II)

The reaction has now been further extended. As one of us is not able to continue the work, the results so far obtained are published.

The following compounds have been prepared: 4′-Methoxy-2 phenylbenzopyrylium ferric chloride (from anisole and coumarin), 3′:4′-dimethoxy-2-phenylbenzopyrylium ferric chloride (from veratrol and coumarin), 4:7-dimethyl-3′:4′-dimethoxy-2-phenylbenzopyrylium ferric chloride (from dimethoxyveratrol and 4:7-dimethylcoumarin), 4:7-dimethyl-2′:4′-dimethoxy-2-phenylbenzopyrylium ferric chloride (from dimethylresorcin and 4:7-dimethylcoumarin).

Experimental.

The general method already described in the previous paper (*loc. cit.*) has been adopted. The mixture of phenol and coumarin in molecular proportions was heated on the water-bath with $POCl_3$ until the mass thickened. It was then treated with ice cold dry ether repeatedly to take away the unacted coumarin and phenol and finally dissolved in strong hydrochloric acid and from the solution the

benzopyrylium ferric chloride compound was precipitated by concentrated solution of $FeCl_3$ and crystallised from glacial acetic acid.

4'-Methoxy-2-phenylbenzopyrylium ferric chloride.—Dark red shining crystals, m.p. 125° (Found: Cl, 32·49; Fe, 12·8. $C_{16}H_{13}O_2FeCl_4$ requires Cl, 32·64; Fe, 12·87 per cent).

3' : 4'-Dimethoxy-2-phenylbenzopyrylium ferric chloride.—Red microcrystals, m.p. 192°. (Found: Cl, 30·42; Fe, 12·20. $C_{17}H_{15}O_3FeCl_4$ requires Cl, 30·54; Fe, 12·04 per cent).

4 : 7-Dimethyl-3' : 4'-dimethoxy-2-phenylbenzopyrylium ferric chloride.—Red microcrystals, m.p. 180°. (Found: Cl, 28·37; Fe, 11·53. $C_{19}H_{19}O_3FeCl_4$ requires Cl, 28·80; Fe, 11·36 per cent).

4 : 7-Dimethyl-2' : 4'-dimethoxy-2-phenylbenzopyrylium ferric chloride.—Dark violet powder, m.p. 150°. (Found: Cl, 29·14; Fe, 10·97. $C_{19}H_{19}O_3FeCl_4$ requires Cl, 28·80; Fe, 11·36 per cent).

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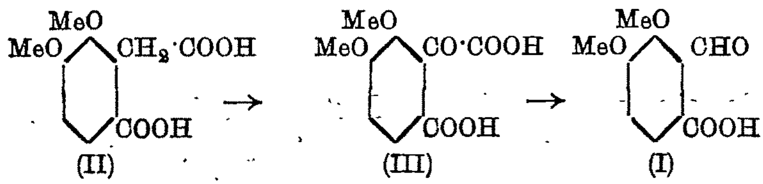
o-Aldehydocarboxylic Acids. Part I. A New General Method of Synthesising Phthalonic Acids. A Synthesis of ψ-Opianic Acid and a New Synthesis of m-Opianic Acid.

By Satyendra Nath Chakravarti and Mahadevan Swaminathan.

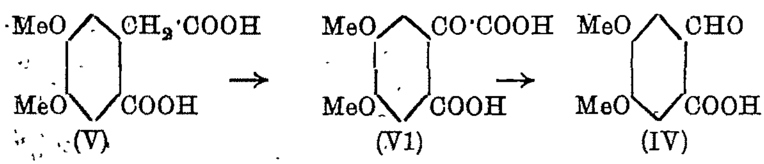
In an earlier paper one of us (S. N. C.) had pointed out that there were very few really good methods available for the synthesis of o-aldehydocarboxylic acids and a new general method of synthesising these acids starting from symmetrically di-and tetrasubstituted derivatives of naphthalene was described (Chakravarti, *J. Indian Chem. Soc.*, 1933, **10**, 693). The difficulty about this new method is that the starting materials for these acids are not yet readily available substances, and we have, therefore, devised another method of synthesising these acids. The method consists in oxidising homophthalic acid with an equimolecular quantity of selenium dioxide in boiling xylene solution when the corresponding phthalonic acid is obtained in excellent yields. The phthalonic acid is then converted into the corresponding o-aldehydocarboxylic acid through its sodium bisulphite compound under the conditions previously described by one of us (*loc. cit.*). Homophthalic acids being readily available substances (*cf.* Perkin and Robinson, *J. Chem. Soc*, 1907, **91**, 1082; Ingold and Pigott, *ibid.*, 1923, **123**, 1476; Haworth, Perkin and Stevens. *ibid.*, 1926, 1764; Chakravarti and Swaminathan, *J. Indian Chem. Soc.*, 1934, **11**, 101), this new method of synthesis would prove to be a valuable one.

ψ-Opianic acid (I), for the synthesis of which numerous unsuccessful attempts have been made in the past (*cf.* Solomon, *Ber.*, 1887, **20**, 888; Perkin and Stoyl, *J. Chem. Soc.*, 1923, **123**, 3178; Edwards, Perkin and Stoyl, *ibid.*, 1925, 196; Chakravarti, *J. Indian Chem. Soc.*, 1929, **6**, 208; Robinson, "On life and work of Perkin", p. 80) and which has been recently obtained by Robinson and Greenwood (*J. Chem. Soc.*, 1932, 187) by the oxidation of β-pseudognoscopine, has now been synthesised by an application of this method. 5:6-Dimethoxyhomophthalic acid (II) was oxidised in boiling xylene solution by means of selenium dioxide to 5:6-dimethoxyphthalonic acid (III). The phthalonic acid was then converted into ψ-opianic acid under conditions described in the experimental section,



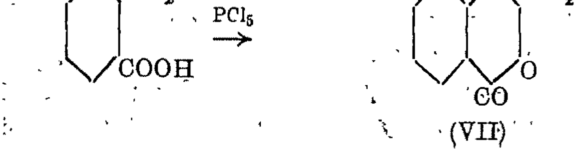
The acid thus obtained had all the properties of ψ-opianic acid obtained by Perkin by the hydrolysis of berberal (*J. Chem. Soc.*, 1890, 57, 1064). For confirmation of its identity it was reduced to ψ-meconine (m p. 124°) and also converted into its oxime (m.p. 125°), and hemipinimide. The mixed melting points of these derivatives with the corresponding authentic specimens showed no depression.

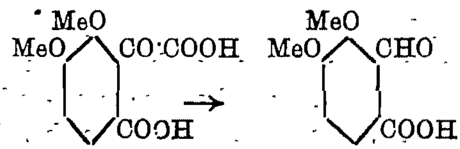
In a similar manner, opianic acid (IV), which had previously been synthesised by tedious methods (*cf.* Fargher and Perkin, *J. Chem. Soc.*, 1921, **119**, 1724; Perkin and Stoyle, *loc. cit.*; Perkin, Edwards and Stoyle, *loc. cit.*), has now been obtained from 4:5-dimethoxyhomophthalic acid (V) in an excellent yield.



A number of other phthalonic acids have been similarly synthesised and an account of the syntheses of all the methoxy and methylenedioxy-*o*-aldehydocarboxylic acids is reserved for a future communication.

Another interesting method of converting homophthalic acids to *o*-phthalaldehydo acids has also been discovered. When a homophthalic acid is treated with 4 molecules of phosphorus pentachloride, a tetrachloro compound is formed which on hydrolysis gives rise to the corresponding phthalonic acid. The latter acid can then be converted into the corresponding *o*-aldehydocarboxylic acid. Thus ψ-opianic acid, which had resisted all previous attempts at synthesis, has now been synthesised in the following manner:—





EXPERIMENTAL.

As a result of a series of comparative experiments, the following condition of oxidation was arrived at as giving the best yield of the phthalonic acids from the corresponding homophthalic acids.

The homophthalic acid (1 mol.) was suspended in dry xylene (generally 100 c. c. for 1 g. of the acid) and the mixture heated to boiling. Selenium dioxide (1 mol.) was then added to the boiling xylene solution and boiling continued for 5 to 8 hours. After the oxidation, the xylene solution and the insoluble residues were thoroughly extracted with dilute sodium carbonate solution and the combined extracts made just acid with concentrated hydrochloric acid and evaporated to dryness on a steam-bath. The residue which contained the free phthalonic acid together with inorganic and other substances were worked up differently in different cases.

The phthalonic acids, which were generally isolated as aniline derivatives or directly converted into *o*-aldehydocarboxylic acids, were obtained thus in yields varying from 50 to 80%. Longer boiling with selenium dioxide in xylene solution or boiling with excess of selenium dioxide did not improve the yields in majority of the cases.

ψ-Opianic acid.—5:6-Dimethoxyhomophthalic acid (5 g.) was suspended in dry xylene (500 c.c.) and the mixture heated to boiling. To the boiling mixture, selenium dioxide (3 g.) was added and the boiling continued for 8 hours. During this process the homophthalic acid gradually went into solution and a reddish solution, containing a black deposit of selenium, was obtained. The mixture was thoroughly extracted with dilute sodium carbonte solution and the combined extracts just acidified and evaporated to dryness. The residue was then taken up in boiling water (50 c.c.), filtered from a little insoluble matter and the filtrate treated with excess of sodium bisulphite solution and evaporated to dryness on a steam-bath and then heated for half an hour at 120° in an air oven. The residue thus obtained was twice stirred up with excess of concentrated hydrochloric acid and evaporated to dryness

on a steam-bath. This residue was then extracted twice with boiling benzene and from the combined benzene extract the solvent removed by distillation. The residual oil was heated on the steam-bath with aniline (4 c.c.) for 10 minutes. On adding a little methyl alcohol and scratching, the aniline derivative separated. On recrystallisation from methyl alcohol, it was obtained as beautiful silky needles, m.p. 187°, yield 1·5 g. (Found: C, 67·3; H, 5·3. The aniline derivative of ψ-opianic acid $C_{16}H_{15}O_4N$ requires C, 67·4; H, 5·3 per cent).

The aniline derivative (1 g.) was heated with dilute hydrochloric acid (10 c.c.) on the steam-bath for 1½ hours. On cooling an acid separated in wooly needles, which on being recrystallised from water and dried on a water-bath melted at 121-22°. (Found: C, 57·5; 57·6; H, 5·0, 5·1. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8 per cent).

The acid was reduced under conditions similar to those used by Perkin for reducing ψ-opianic acid to ψ-meconine, when a substance, m.p. 124°, identical in all respects with ψ-meconine, was obtained.

On treatment with hydroxylamine hydrochloride under conditions described by Perkin (*loc. cit.*), it gave rise to an oxime, m.p. 124°, identical with the oxime of ψ-opianic acid.

5 : 6 - *Dimethoxy* - 3 : 3 : 4 : 4 - *tetrachloro* - 3 : 4 - *dihydroisocoumarin* (VII).—5 : 6-Dimethoxyhomophthalic acid (3·6 g.), mixed with phosphorus pentachloride (12·5 g.) and phosphorus oxychloride (5 g.) was heated for 8 hours at 140-150°. The phosphorus oxychloride was removed under reduced pressure from a water-bath and the residue was treated with cold water, when a solid separated. This solid on crystallisation from methyl alcohol gave (VII) in beautiful prisms, m.p. 128°, yield 0·8 g. (Found: C, 38·3, 38·37; H, 2·46, 2·41; Cl, 40·96, 41·0. $C_{11}H_8O_4Cl_4$ requires C, 38·2; H, 2·3; Cl, 41·0 per cent). This chloro compound is readily soluble in ordinary solvents and is remarkably stable towards water and methyl alcohol.

Conversion of (VII) *to ψ-opianic acid.*—The tetrachloro*iso*coumarin (1 g.) was added to methyl alcoholic potash (2 g. dissolved in 50 c.c. of methyl alcohol) and refluxed for 8 hours on the steam bath. The methyl alcohol was then completely removed and the residue dissolved in water. The solution was made just acid and evaporated to dryness. The residue was taken up in 10 c.c. of 40 % sodium bisulphite and the sodium bisulphite compound on being treated in the manner described earlier gave an aniline derivative (0·6 g.), m.p. 187°, and an aldehydo-acid, m.p. 121-22°, which were

found to be identical with the aniline derivative of ψ-opianic acid and with ψ-opianic acid respectively, and the mixed melting points showed no depression.

m-*Opianic acid*—(*i*). 4:6-Dimethoxyhomophthalic acid (5 g.) was oxidised with selenium dioxide under conditions described in the case of 5:6-dimethoxyhomophthalic acid and crude phthalonic acid, obtained in the manner described under the general method, was taken up in 100 c.c. of boiling water and treated with aniline (4 c.c.). The mixture was heated for ½ hour when the aniline salt of 4:5-dimethoxyphthalonic acid separated in an excellent yield (4 g.). The aniline derivative crystallises from methyl alcohol in glistening laminae, m.p. 179-80°. The aniline derivative on being treated in the manner described for *m*-opianic acid by Perkin and Fargher (*loc. cit.*) gave an acid, m.p. 187-88°, which was identical in all its properties with *m*-opianic acid. (Found: C, 56·7; H, 5·0. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8 per cent).

(*ii*) When the oxidation in xylene solution was carried out for 8 hours and the product worked up as before, the yield of the aniline derivative was 5 g.

)*iii*) When the oxidation was continued for 16 hours, the final yield was a little over 5 g.

Oxidation of homophthalic acid.—Homophthalic acid was prepared according to the method described by Ingold and Pigott (*loc. cit.*) and oxidised under 3 different conditions described in the previous case. The following yields of the aniline derivative of the phthalonic acid were obtained:—

(*i*) Boiling in xylene solution with selenium dioxide for 3 hours. From 5 g. of the homophthalic acid 3 g. of the aniline derivative, m.p. 166°, was obtained.

(*ii*) When the boiling was continued for 8 hours, the yield of the aniline derivative was 2·5 g.

(*iii*) When the boiling was continued for 16 hours, the yield of the aniline derivative was reduced to 2 g.

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Some Indian Acorn Oils (*Quercus incana*, Roxb., *Q. dilatata*, Lindl., and *Q. ilex*, Linn.).

By S. V. Puntambekar and S. Krishna.

Quercus grow all over the hills in Northern India and yield acorns in great abundance. At present these find no commercial application because of the low percentage of oil in the kernel and the poor quantity of the tanning material in the 'acorn cups' ('Valonia' of trade). In view of the absence of any chemical data on the oils (with the exception of *Q. agrifolia*—Blasdale, *J. Amer. Chem. Soc.*, 1895, **17**, 935) it is considered desirable to place on record our findings.

Of about thirty species which occur in India, *Q. incana*, Roxb. Vern. *Banj* (Punjab) is probably the most common and the best known and the oil from this was, therefore, investigated in detail. The acorns were sent to us from Wazirstan (N. W. F. Prov.).

The kernels (81%) on separation from the shells were dried, powdered and extracted for the oil in a Soxhlet with petroleum ether. In this way 16% of the oil were obtained which after complete removal of the solvent under vacuum was employed for the determination of its constants.

		Q. incana.	*Q. dilatata.*	*Q. ilex.*
Consistency	...	Thin	Thin	Thin
Colour	...	Yellow	Orange	Orange
Sp. gr. at 25°	...	0·9081	0·9084	0·9079
Refractive index at 30°	...	1·4576	1·4588	1·4576
Saponification value	...	192·2	188·4	189·9
Iodine value (Hanus)	...	81·5	90·3	88 0
Acetyl value	...	14·8	21·1	17·4
Hehner value	...	96·1	88·2	94·9
Acid value	...	13·0	22·2	8·5
Unsaponifiable matter	...	0·8%	2·3%	0·9%

Composition of the Fatty Acids (incana oil).

After removal of the unsaponifiable matter the mixed fatty acids were separated into solid and liquid acids by the Twitchell's method and both these acids were further divided into their components by the fractional distillation of their methyl esters.

Chemical constants of the mixed fatty acids.

Mean molecular weight	285·2
Iodine value (Hanus)	80·8
Saturated acids	18·0%
Unsaturated acids	82·0%

Saturated acids.—150·7 G. of the mixed acids, from which the unsaponifiable matter had been removed, gave the following fractions after performing the Twitchell's operation twice.

Acids.	Iodine value.	M.W.	Net weight.
S—solid	0	268·1	19·1 g.
S_A—solid	43·6	302·0	2·4
L—liquid	85·3	288·0	129·2

Solid acids (S) were converted into their methyl esters and 20·4 g. of the dry neutral esters were fractionated at 3-5 mm. The liberated acids from each fraction were fractionally crystallised for identification of their components.

Fractions.	B.p.	Weight.	M.W. of the acids.	Component of the esters. Methyl palmitate	Methyl lignocerate.
S_1	168-70°	13·83 g.	254·3	13·83 g.	...
S_2	170-75	3·30	265·4	3·02	0·28 g.
S_3	175-85	1·47	275·0	1·22	0·25
Residue	>185°	1·50	282·3	1·15	0·35
Loss	...	0·30			
Total		20·40		19·22	0·88

Fraction S_1 melted at 28-30° and the liberated acids on crystallisation from acetone gave a product (m.p. 61-62° and M.W. 254) which was identified as palmitic acid by its mixed melting point with an authentic sample.

Fraction S_2 melted at 26-28° and the liberated acids had a m p. of 56-57° and a M.W. of 265·4. Two crystallisations from acetone raised the M.W. to 267 but did not alter the m.p. indicating the fraction to consist mostly of palmitic acid and a small portion of an acid (possibly lignoceric) of higher molecular weight.

Fraction S_3—The acids from this fraction on crystallisation gave a product m. p. 56-58° and M. W. 282·6. Further crystallisation did not appreciably improve the purity of the acids which again appear to be a mixture of palmitic and perhaps lignoceric acids.

The residue on thrice crystallisation gave the following products :

Crystallisation	M.p	M.W.
1	60-61°	318·2
2	63-64	...
3	68-69	340·6

The amount of acids at this stage being small, further crystallisations were not attempted. The above results show that at no stage do the m.p. and the M.W. agree to those of pure acids (palmitic, stearic, arachidic and behenic). Comparatively high M.W. and the correspondingly low m.p. of the products, however, indicate the residue to be mainly a mixture of acids of high and low molecular weights such as palmitic and and lignoceric but not of two consecutive acids such as palmitic and stearic or stearic and arachidic and so on. Though no lignoceric acid has actually been isolated yet for purposes of calculations its presence has been assumed.

The above results indicate that the solid acids consist mainly of palmitic acid together with a small amount of an acid, such as lignoceric acid, of high molecular weight.

Fraction S_A—The amount of these acids was too small for fuller identification. On dissolving in petroleum ether they produced turbidity. This fact coupled with their appreciable iodine value and high M. W. indicates that besides oleic and palmitic acids they contain a small amount of hydroxylated product such as dihydroxystearic acid.

Unsaturated Acids.

The liquid acids (L) were saponified to break up the esters which might have been formed in the alcoholic treatment. The slightly lower iodine value and the higher M. W., when compared with those for ordinary oleic acid, indicate that the acids contain some saturated acids.

A portion of the acids was converted into its potassium soap and oxidised by a dilute potassium permanganate solution according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, **127**, 1628). The oxidised product was identified as dihydroxystearic acid (m. p. varying from 120-132; M. W. 316) and the unoxidised portion (7 0%) was left as a viscous mass of mean M. W. 278·0 and iodine value 7·3. Another portion was oxidised after being converted into potassium soap by a concentrated solution of potassium permanganate according to the modified method of Hilditch and Priestman (*Analyst*, 1931, **56**, 354). The unoxidised acids obtained after magnesium salt separation (5·0 %) melted at 53-54° and had a M. W. 280·2 and iodine value zero.

The above oxidation experiments indicate that the unsaturated acids in the liquid acids (L) consist entirely of oleic acid with the possible presence of some of its isomers and that the acids of more than one double bond namely, linoleic etc. are absent. They also prove that the liquid acids still retain a small amount of solid acids probably palmitic acid (a fact is also borne out by the iodine value of the liquid acids). The higher molecular weight is in all probability due to the incomplete removal of the dihydroxystearic acid (Jay, *J. Soc. Chem. Ind.*, 1932, **51**, 126 T).

The remaining portion of the liquid acids was converted into methyl esters in the usual way and 110 g. of these were fractionally distilled at 3-5 mm. pressure with the following results.

Fractions.	B. p.	Weight.	Iodine value.	Component of the esters. Methyl palmitate.	Methyl oleate or isomers.
L_1	50-175°	2·34g.	52·0	0·92	1·42
L_2	175-180°	41·13	80·2	2·67	38·46
L_3	180-183°	44·00	85 5	—	44·00
L_4	183-186°	8·05	78·0	—	8·05
Residue		13·07	57·0	—	13·07
Loss		1·41	—	—	—
Total		110·00	—	3·59	105·00

Fraction L_1.—The acids from this when liberated and dried set to a viscous mass, the dilute alcoholic solution from which on cooling

yielded a small amount of acid, m. p. 55-56°. This appeared to be palmitic acid. The amount being small further purification was not attempted.

Fraction L_2.—The iodine value indicated this fraction to contain a small amount of a saturated substance, evidently methyl palmitate, but it could not be isolated.

Fraction L_3.—This is wholly methyl oleate.

Fraction L_4.—The low iodine value indicates that either the esters must have been polymerised to some extent or that they contain some isomer or isomers of methyl oleate of low iodine value and higher b. p. The varying m. p. of the dihydroxystearic acid obtained in Lapworth's oxidation experiment supports this assumption. It is quite possible that in nature the oleic acid is more often associated with its isomers than is commonly realised. It also appears not unlikely that this fraction contains a small amount of oxidised methyl oleate (Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, **10**, 210) which, however, was not isolated. The residue was a very dark viscous mass containing mostly the polymerised and degradation products of methyl oleate and almost all the colouring matter of the mixed acids.

The above results of the fractional distillation of the methyl esters of the solid and liquid acids on calculation gave the following percentage composition for the fatty acids.

Acids.	Weight.	Percentage.
Palmitic	25·9 g.	17·1
Lignoceric (?)	1·2	0·9
Oleic	123·6	82·0

Unsaponifiable matter.—Since the attempts to crystallise the sterols from the alcoholic solution of the unsaponifiable matter, obtained from the mixed fatty acids in the usual manner, was not successful, they were precipitated with 1% solution of digitonin in alcohol. As the amount of the precipitated digitonide was very small it was directly converted to sterol acetate by refluxing it with acetic anhydride. The purified sterol acetate melted at 126-28° and is apparently the acetate of the common phytosterol, sitosterol, found in vegetable oils.

The residue from the mother liquor was taken up in boiling xylene and filtered. The material obtained after the complete removal of the solvent was a viscous mass, iodine value 59·2. It burns with a smoky flame but is soluble in cold concentrated sulphuric acid. These facts indicate it to be an unsaturated hydrocarbon or a mixture of such hydrocarbons. The material being very little further identification was not possible.

Summary.

The oil from the acorn kernels of *Quercus incana* has been found to contain the glycerides of palmitic, lignoceric and oleic acids and a small amount of sitosterol.

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Received May 15, 1934.

Photosynthesis of Amino Acids.

By N. R. Dhar and S. K. Mukherji.

It is generally believed by plant physiologists that synthesis proteins in plants can take place even in the dark, provided carb drates are available and nitrogen assimilation by plants is nc photochemical process.

In order to test this point, we have tried to synthesise *in* amino acids by exposing to sunlight solutions of glucose or gl and nitrates in presence of different catalysts and photosensiti and results are recorded in this paper. The detection and estima of amino acids have been satisfactorily described by Mitchell Hamilton ("Biochemistry of Amino Acids," 1929).

Small amounts of amino acids can be detected and estim colorimetrically by the triketohydrindene hydrate, also known "ninhydrin"

$$C_6H_4 \left\langle {CO \atop CO} \right\rangle C\,(OH)_2.$$

A blue colour develops when this reagent is m with an amino acid containing one free carboxyl and free amino group in the α-position and the mixture hea This reaction is sensitive to the extent of one part of an α-an acid dissolved in 15,000 to 80,000 parts of water. With ammon hydroxide and ninhydrin, a yellow or red colour is obtained. Am nium salts, urea, uric acid and hippuric acid form a faint ye coloration with ninhydrin. Concentrated solutions of alcol aldehydes, ketones and reducing sugars cause a red colour with hydrin and this disappears on cooling or dilution. The blue co produced with amino acids and ninhydrin, appears to be of coll nature and hence in this test an excess of neutral salts has to avoided. Addition of pyridine seems necessary as it acts as a bu and keeps the colouring matter in solution. With this valuable reag the amounts of amino acids obtained photosynthetically could estimated colorimetrically by a Duboscq colorimeter according to method of Harding and McLean (*J. Biol. Chem.*, 1915, **20**, 217 ; 1 **24**, 503). The test is ordinarily applied in the following way Dissolve 0·1 g. ninhydrin in 100 c.c. of water and prepare a 10% s

tion of pyridine in water. 1 C.c. of the solution containing the amino acid is mixed with 1 c.c. of the ninhydrin solution and 1 c.c. of the pyridine solution and the mixture heated in a test tube in boiling water for 20 minutes and if an amino acid is present, a bluish or bluish violet colour develops. On comparing the tint obtained with a standard solution of glutamic acid, which is quite stable in the dark, the amount of amino acids photosynthesised could be estimated. The glutamic acid (B.D.H.) used in these experiments, was free from glucose and other impurities and was pure as determined by its melting point (197-98°).

$N/2$ solutions of different nitrates (100 c.c) and glucose (5 g.) were exposed to sunlight in open 250 c.c. pyrex glass beakers and it was observed that in the absence of a photosensitiser, practically no amino acid is obtained. Amongst the photosensitisers, titania is the best ; uranium ammonium carbonate acts as a feeble photosensitiser in the formation of amino acid from nitrates and glucose. In the following experiments, 1 g. of titania was added and the mixture stirred from time to time and 5 c.c. of the solution withdrawn and filtered and the amino acid formed was estimated colorimetrically by adding ninhydrin. The following results have been obtained.

TABLE I.

Time.	Amounts of amino acid formed with		
	$N/2$-NH_4NO_3.	$N/2$-$NaNO_3$.	$N/2$-KNO_3.
2 hr.	0	0	0·00012N
4	0·00005N	0·00027N	0·00040
6	0·00125	0·00040	0·00084
8	0·00109	0·00024	0·00110
10	0·00053	0·00020	0·00034
12	0·00000	0·00018	0·00027
Dark	0	0	0

The foregoing results show that the amount of α-amino acids photosynthesised from glucose and nitrates in presence of titania, is maximum with ammonium nitrate and minimum with sodium nitrate. Moreover, the amount of α-amino acids photosynthesised reaches a maximum value with increase of exposure and then falls off on further exposure. After 15-20 hours' exposure, practically no amino acid is detected, probably due to their photo-oxidation. It is interesting to note that no amino acid is obtained from glucose and

nitrates and titania when kept in the dark for several days, but in diffused light, appreciable amounts of amino acids are formed in open shallow porcelain dishes. When $N/2$-NH_4OH or NH_4Cl or $N/2$-$(NH_4)_2 SO_4$ is substituted for nitrates, no amino acid is photosynthesised in this way, although plants like barley, rice, maize and pumpkins, which are rich in carbohydrates, readily take up ammonium salts.

The effect of the addition of differently coloured inorganic salts (0·5 g. in each case) to a mixture of glucose (4%), $N/2$-potassium nitrate and titania (1 g.) was also investigated and the results are as follows.

TABLE II.

Time⟶	4 hrs.	8 hrs.	12 hrs.	Dark
Uranium acetate	0·00014 *N*	0·00054 *N*	0·00007 *N*	0
Cobalt chloride	0·00014	0·00058	0·00007	0
Copper sulphate	0·00013	0·00040	0·00005	0
Nickel sulphate	0·00013	0·00040	0·00005	0
No coloured salt	0·00012	0·00035	0·00003	0

These results show that increased light absorption by the mixtures, increases the amounts of amino acid photosynthesised.

The results in Table III show that ferrous sulphate increases the yield of amino acid but sodium phosphate or calcium carbonate is without any influence.

TABLE III.

0·5 G. of each reagent added.

Time.	Sodium phosphate.	Calcium carbonate.	Ferrous sulphate.	No reagent.
4 hr.	0·00014*N*	0·00014*N*	0·00021*N*	0·00014*N*
6	0·00021	0·00021	0·00028	0·00021
8	0·00035	0·00035	0·00049	0·00034
10	0·00035	0·00035	0·00028	0·00034
12	0·00014	0·00014	0·00008	0·00014
Dark	0	0	0	0

It seems that the photo-oxidation of amino acids on prolonged exposures is facilitated by ferrous sulphate, as the amounts of amino acids decrease more readily in its presence when the exposure is prolonged.

In the following tables, the influence of the variation in the amounts of nitrates, glucose and titania has been investigated.

TABLE IV.

4 G. of glucose and 1 g. TiO_2 used.

Exposed for →	6 hrs.	8 hrs.	10 hrs.
$N/2{\cdot}5$-KNO_3	0·00035N	0·00034N	0·00027
$N/5$	0·00035	0·00033	0·00029
$N/10$	0·00035	0·00032	0·00031
$N/20$	0·00034	0·00032	0·00032
$N/40$	0·00029	...	0·00035
$N/80$	0·00029	...	0·00022
$N/160$	0	...	traces
$N/320$	0	...	0

TABLE V.

2 G. of KNO_3 and 1 g. of TiO_2 used.

	glucose (g.) ...	4	2	1	0·5	0·25	0·125	0·0625
Time	6 hrs. ...	0·00039N	0·00035	0·00028	0·00022	0·00014	0·00007	0·00003
	8 hrs.	0·00060N	0·00030	0·00007	0	0	0	0

2 G. of Glucose and 1 g. of KNO_3 used.

	TiO_2 (g.) ...	3	2	1	0
Time	6 hrs. ...	0·00039N	0·00035	0·00028	0·00007
	8 hrs. ...	0·00051N	0·00019	0·00042	0·00022

The results recorded in Tables IV and V show that after the limiting concentration $N/80$, the amount of amino acid photosynthesised increases slightly with increase of potassium nitrate concentration. When the concentration of KNO_3 is $N/160$ or smaller, practically no amino acid is photosynthesised.

The amount of amino acid produced increases appreciably with increase in the glucose concentration. Increase of titania also increases the photosynthesis.

In order to find out whether the products of the reaction affect the activity of the titania surface, the following experiments were

performed. Three beakers A, B, C each containing 2 g. of glucose, 2 g. of KNO_3 and 1 g. titania were exposed to sunlight. The beaker A was left undisturbed. The solution in beaker B was changed after 8 hours' exposure and fresh solution of the same concentration was put in. In beaker C, after 8 hours' exposure, the titania was replaced by the same amount of fresh titania. The amounts of amino acid photosynthesised are recorded in Table VI.

TABLE VI.

	Time → 8 hrs.	12 hrs.	14 hrs.
A. Glucose (2 g.) + KNO_3 (2 g.) + TiO_2 (1 g.)	0·00035 N	0·00022 N	0·00007 N
B. Same TiO_2 but new solution after 8 hrs.	—	0·00007	0
C. Same solution but fresh TiO_2 after 8 hrs.	—	0·00043	0·00049

It seems that the surface of titania in contact with the exposed solution becomes ineffective probably due to the adsorption of the products of the reaction.

Not only glucose but fructose, mannose, galactose and arabinose when exposed to sunlight with potassium nitrate and titania yield amino acids. Moreover, substances, which on exposure to light form reducing sugars readily, also produce amino acids with KNO_3, as is evident from the following table.

TABLE VII.

$N/2$-KNO_3 and 1 g. of TiO_2 with 5% solutions of the following.

Time	Tartaric acid.	Glycerol.	Glycol.	Lactic acid.	Citric acid.	Malic acid.
8 hrs.	0·00039 N	0·00046 N	0·00036 N	0	0	0
12 hrs.	0·00001 N	0·00002 N	0·00002 N	0	0	0

With lactic, citric and malic acids, reducing sugars can be detected by Fehling's or Benedict's solution only after long exposures, whereas with glycerol, glycol and tartaric acid, sugars are detected even after an exposure of 30 minutes with potassium nitrate and titania.

It is known that ammonium lactate forms alanine in the animal body. On exposing 3% solution of ammonium lactate with titania, amino acid is detected after five hours. On the other hand, ammonium tartrate, ammonium malate, ammonium citrate and

a mixture of ammonia and glycerol even after 30 hours' exposure to sunlight do not produce any amino acid.

Attempts were made to isolate the amino acids formed in photosynthesis from (*a*) mixtures of 50 c. c. glycol and 20 g. of potassium nitrate, and (*b*) mixtures of 20 g. glucose and 20 g. of potassium nitrate in presence of 10 g. of titania per litre of solution exposed in open shallow porcelain dishes to sunlight for 6—8 hours. It was suspected that glycine would be formed from glycol and arginine from glucose.

(*a*) *With glycol.*—The exposed solution was filtered to free it from titania and was concentrated under vacuum on a water-bath. The amount of amino acid formed was estimated colorimetrically and an equivalent amount of sodium carbonate was added and followed by the addition of excess of mercuric acetate solution and a stream of CO_2 was passed. The precipitate obtained was filtered and to the solution, alcohol was added to precipitate the mercury salt of glycine carbonate, which was first washed thoroughly with alcohol and then with cold distilled water. H_2S was passed to liberate the amino acid and the excess of H_2S removed by a current of hydrogen. On evaporation glycine separates out (*cf.* Neuberg and Kerb, *Biochem. Z.*, 1912, **40**, 498; Siegefried Schutt, *Z. physikal. Chem.*, 1912, **72**, 260). This method yields the amino acid, which has to be further purified by dissolving it in water and treating the solution with alcohol and $Ba(OH)_2$ and a stream of CO_2 (*cf.* Kingston and Schryver, *Biochem. J.*, 1924, **18**, 1070). The precipitate was filtered and washed with alcohol and then with cold water. The glycine was extracted with hot water from the barium carbonate, which was filtered off. On evaporation, crystals were left.

The amino acid gave a strong blue coloration with ninhydrin and a red coloration with ferric chloride and a blue colour with phenol and sodium hypochlorite. These are important tests for glycine. The meling point of the crystals varied from 220° to 228° (m. p. of glycine, 225°—230°). Glycine forms a soluble copper salt, which was prepared and dried and ignited and weighed as CuO. From 0·1170 g. of the copper salt 0·0385 g. CuO was obtained in one experiment giving a molecular weight of 80·1 for the amino acid (theoretical 75).

(*b*) *With glucose.*—As in the former case (*cf.* Neuberg and Kerb, *loc. cit.*) the amino acid was first purified by decomposing the mercury salt with H_2S; but in this case, the amino acid is

contaminated with glycuronic acid. To purify the amino acid further, flavianic acid was added to the solution and kept in the cold for 3 days. The crystals obtained were washed in cold water and again purified by recrystallisation. The melting points of different samples varied from 257° to 270°, when there was carbonisation. The m. p. of arginine flavinate is about 260° (*cf.* Kossel and Gross, *Z. physiol. Chem.*, 1924, **135**, 167).

In order to isolate the amino acid, the flavinate was dissolved in 33% hot H_2SO_4 and the sulphonic acid was removed by extraction with butyl alcohol. The aqueous solution was treated with $Ba(OH)_2$ in excess and saturated with CO_2 and filtered. The filtrate on evaporation yields an amino acid, which sinters at 234° and carbonises at 240° and gives the tests for arginine. Further work on the isolation of the amino acids in the pure state is in progress.

The experimental results recorded above show that small amounts of amino acids are readily formed *in vitro* by the interaction of nitrates and carbohydrates, or substances which produce carbohydrates, readily when exposed to sunlight in presence of suitable catalysts and photosensitisers and no amino acid is synthesised in the dark.

In plants, not only six membered carbohydrates but six membered amino acids, such as leucine, arginine, lysine, histidine, tryptophan and cystine chiefly occur in plant proteins. Amongst the amino acids obtained from the plant proteins, arginine occurs in the largest amount. We have been able to obtain evidence of arginine formation from glucose and nitrates and titania in presence of sunlight. It seems, therefore, that the amino acids in plants are synthesised from carbohydrates and nitrates and that sunlight is an important agency in this reaction and the plant pigments are likely to behave as sensitisers, just as titania and uranium salts sensitise the process *in vitro*.

In previous publications (*J. Indian Chem. Soc*,, 1933, **10**, 287, 699) it has been observed that aqueous solutions of amino acids are readily oxidised to ammonia and carbon dioxide and other products in presence of light and air. It appears, that the amino acids obtained in photosynthesis are oxidised by potassium nitrate or oxygen of the air in presence of sunlight and thus the photosynthesised amino acids disappear on longer exposure.

Recently it has been observed by us that the constancy C:N ratio (10:1) not only exists in the soil but is also observed in animal

metabolism and when a mixture of organic compounds containing nitrogenous substances present in natural systems undergo oxidation in air, a constant ratio of carbon to nitrogen is finally attained (results communicated to this journal for publication).

In the plant, protein synthesis takes place only when carbohydrates are present, because the reaction between nitrate and carbohydrate causes the liberation of energy, which seems to be indispensable for protein synthesis and that is why most plants cannot utilise ammonium salts directly because of the lack of the energy available from the reaction of the carbohydrates and nitrates. It has been stated that the rice plants take up ammonium salts in the beginning of its development and nitrates in the end. It seems that in the case of rice and other carbohydrate producing plants, in the beginning they contain large amounts of carbohydrate and little protein and thus the C:N ratio may be much greater than 10:1 and hence the ammonia is absorbed; whilst in the end, protein accummulation takes place due to the energy supplied by the oxidation of the carbohydrates and then the ratio of C:N tends to the value 10:1 and that is why ammonium salts are not required. Legumes, lupins and beans, however, should at no stage grow with ammonium salts. On the other hand, starch and other carbohydrate producing plants at certain stages, when the carbohydrate content is very high and protein content low, may be fed and made to grow well by ammonium salts.

It is stated that the case of ammonia assimilation by plants depends on the rate with which it is converted into asparagine and this in turn depends on the amount of carbohydrates, the other class of substances necessary for protein synthesis.

SUMMARY.

1. Small amounts of α-amino acids are photosynthesised by exposing solutions of glucose and nitrates in presence of titania to sunlight. The yield is greater with nitrates of ammonium and potassium than sodium. Longer exposure causes the disappearance of the amino acids, due to their photo-oxidation.

2. Coloured inorganic salts cause an increase of photosynthesis but $CaCO_3$ and sodium phosphate are without influence.

3. Increase in the amounts of glucose or titania causes more photosynthesis than an increase in the amount of KNO_3. Other carbohydrates such as fructose, galactose, arabinose etc., and

substances which on exposure to light produce reducing sugars yield also readily, amino acids. Ammonium lactate on exposure to light with tatania forms amino acid.

4. It seems that glycine from glycol and KNO_3 and TiO_2, and arginine from glucose, KNO_3 and TiO_2 are formed along with other substances from photosynthesis and attempts have been made to isolate these two amino acids.

5. It has been found that *in vitro* ammonium salts and carbohydrates do not form amino acids in light. It seems that protein synthesis in plants and *in vitro* is facilitated by the energy obtained from the oxidation of carbohydrates by nitrates or oxygen of the air. An explanation has been offered why carbohydrate-producing plants can grow in the presence of ammonium salts, and it is believed that the absorption of ammonium ion or nitrate ion by a plant is controlled mainly by the ratio C : N in it.

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Varying Valency of Platinum with respect to Mercaptanic Radicals. Part VIII.

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A good number of compounds by the interaction of chloropla acid with various organic thio compounds (sulphides, mercapt disulphides, etc.) has already been described by Rây and workers (*J. Chem. Soc.*, 1919, **115**, 872; 1922, **121**, 1 1923, **123**, 133; *J. Indian Chem. Soc.*, 1925, **2**, 178). action of various bases on some of these complex bodies to eluci their constitution has also been investigated (*cf.* Rây collaborators, *J. Indian Chem. Soc.*, 1926, **3**, 155, 358; 1927, **4**, 1928, **5**, 139).

In the present paper the action of another organic thio compo which may be called a 1:4-disulphide, on chloroplatinic acid been studied and the compound thereof and its derivatives have subjected to the action of bases (like ethylenediamine, ammonia pyridine). The resulting products are of much value in elucida the constitution of the platinum disulphide complexes most of w are insoluble in common solvents.

The 1:4-disulphide employed in preparing platinum compl has the constitutional formula, Et $S \cdot CH_2 \cdot CH_2 \cdot S \cdot$ Et (*cf.* Ma *Ber.*, 1884, **19**, 3266).

By the action of the disulphide upon H_2PtCl_6, a substanc the approximate composition of $PtCl_3 \cdot C_6H_{14}S_2$ has been obtai This insoluble substance (P) may be either $PtCl_3 \cdot C_6H_{14}S_2$ (*cf. J. Indian Chem. Soc.*, 1928, **5**, 139) or a molecular comp of $PtCl_4$, $C_6H_{14}S_2$ (B) and $PtCl_2 \cdot C_6H_{14}S_2$ (C) (*cf. ibid.*, 1 2, 178) or may be a mixture of (B) and (C) in equimolec proportions approximately. However, the insolubility of the s tance (P) in all ordinary solvents prevents its purification or separation of (B) and (C), if it be a mixture. But both the c pounds (B) and (C) have been obtained from (P) (*vide* experime by oxidation and reduction respectively, of which (C) is soluble acetone. The substance (P) on continued boiling with aceton a water-bath for a few hours gives an acetone extract which le

almost nothing on evaporation. This shows that (P) is not a mixture but a distinct chemical compound (with slight impurities) which may be either (A) or the molecular compounds of (B) and (C).

However, by the action of ethylenediamine on the substance (P), a compound $PtCl_2 \cdot En_2$ (m.p. 308°d.) of known constitution $(PtEn_2)$-Cl_2 has been obtained by replacing completely the disulphide molecule (*cf.* Jorgensen, *J. pr. Chem.*, 1899, *ii*, **39**, 4, 1949). The formation of the above compound can be explained by supposing the mother substance (P) either as (A) (*cf. J. Indian Chem. Soc.*, 1928, **5**, 467) or as the molecular compound of (B) and (C) (*cf.* the action of NH_3 on $PtCl_3$, $2Et_2S$ *ibid.*, 1926, **3**, 155), but both (B) and (C) form the same compound $PtCl_2 \cdot En_2$ separately with ethylenediamine.

The action of a base of the pyridine type on the substance (P) on continued reflux on a water-bath gives two componnds, one of which has been identified as $[PtPy_4]Cl_2$ (m.p. 285°d.), while the other one has approximately the empirical formula $PtCl_3 \cdot 2Py$; but it could not be obtained in a purer state owing to its insolubility in ordinary solvents. From these results, the molecular formula of (P), though not definitely established, is probably of $PtCl_3 \cdot C_6H_{14}S_2$.

The action of dimethylaniline on the substance (P) leads to $[Cl_2 \cdot Pt \cdot C_6H_{14}S_2]$ (m.p. 187°) which is soluble only in acetone unlike the original substance (P) (Drew and Wyatt, *J. Chem. Soc.*, 1934, 56).

When $PtCl_2 \cdot C_6H_{14}S_2$ is treated with ethylenediamine or with pyridine, the compound $PtCl_2 \cdot En_2$ (m.p. 308°d.) or $PtCl_2 \cdot 4\,Py$, (m.p. 285°d.) (*cf.* the action of ethylene diamine and pyridine on $PtCl_2 \cdot C_6H_{14}S_2$) is obtained. The formation of these compounds from $PtCl_2 \cdot C_6H_{14}S_2$ supports the molecular formula for $PtCl_2 \cdot C_6H_{14}S_2$.

The action of a mild oxidising agent, *e.g.*, the mixture of hydrochloric acid and hydrogen peroxide on $PtCl_3 \cdot C_6H_{14}S_2$ converts the latter into $[Cl_4 \cdot Pt \cdot C_6H_{14}S_2]$.

The action of ethylenediamine on $[Cl_4 \cdot Pt \cdot C_6H_{14}S_2]$ forms the compound $PtEn_2Cl_2$ (m.p. 308°d.) and with ammonia, a well known compound of similar type $[Pt \cdot 4NH_3]Cl_2$ (Carlgreen and Cleve, *Z. anorg. Chem.*, 1892, **1**, 67).

But when the substance $[Cl_4 \cdot Pt \cdot C_6H_{14}S_2]$ is treated with pyridine, a compound of a different type $[Cl_4 \cdot Pt \cdot Py_2]$ is obtained which is insoluble in ordinary solvents,

This supports the constitution of $PtCl_4 \cdot C_6H_{14}S_2$ as given above; pyridine only replaces the disulphide molecule, whereas bases like ammonia and ethylenediamine not only replace the disulphide molecule, but also transform, the 6-co-ordinate platinum to a 4-co-ordinate one.

EXPERIMENTAL.

Action of chloroplatinic acid on the disulphide, $Et \cdot S \cdot C_2H_4 \cdot S \cdot Et$.—To a strong alcoholic solution of chloroplatinic acid (8 g.) dilute alcoholic solution of the disulphide (3 g.) was added and the mixture gently shaken. The reaction began instantaneously with the separation of an orange coloured insoluble substance which on keeping overnight, was found to be a semi-solid mass. It was transferred on a filter under suction. The residue on the filter was repeatedly washed with alcohol, hot water, alcohol and finally with ether and dried in vacuum. This substance was found to be insoluble in all ordinary solvents, m.p. 168—71° (d.) (I). The main filtrate gave another crop after 24 hours and the second crop was isolated as before, m.p. 175-78° (d.) (II). In the same way, the third crop was also obtained, m.p. 180-82° (d.) (III). All the crops were flesh-coloured and isoluble in ordinary solvents and correspond approximately to the formula $PtCl_3 \cdot C_6H_{14}S_2$. [Found: (I) Cl, 24·07; S, 14·39; Pt 42·7. (II) S, 14·08; Pt, 42·5. (III) S, 14·47; Pt, 42·02. $PtCl_3 \cdot C_6H_{14}S_2$ requires Cl, 23·58; S, 14·17; Pt, 43·18 per cent].

Action of ethylenediamine on $PtCl_3 \cdot C_6H_{14}S_2$.—Ethylenediamine hydrate (5 c.c.) was added to $PtCl_3 \cdot C_6H_{14}S_2$ (5 g.) in water suspension (20 c.c. of water). After keeping the mixture for 2 days in a closed flask, the whole of $PtCl_3 \cdot C_6H_{14}S_2$ went into solution with ether. The aqueous solution thus remained was concentrated to a small volume in a vacuum desiccator over sulphuric acid and precipitated with alcohol. The first crop was precipitated with alcohol and finally crystallised from rectified spirit. This is necessary to free the substance from the hydrochloride of the base that might be formed in the reaction. The substance was brownish in colour m.p. 308° (d.). [Found : N, 14·16; Pt, 50·48. $PtCl_2 \cdot 2C_2H_4(NH_2)_2$ requires N, 14·51; Pt, 50·61 per cent].

Action of pyridine on $PtCl_3 \cdot C_6H_{14}S_2$.—$PtCl_3 \cdot C_6H_{14}S_2$ (5 g.) in alcoholic suspension (25 c.c. alcohol) was refluxed on a water-bath with pyridine in excess (10 c.c.) for 56 hours. The mixture was filtered hot; the filtrate on cooling deposited a crystalline substance which was filtered off and washed several times with ether. The substance is soluble in water, turns yellow at 120°, m.p. 285° (decomp.). (Found: N, 9·34; Cl, 11·9; Pt, 33·62. $PtCl_2 \cdot 4\ C_5H_5N$ requires N, 9·62; Cl,12·19; Pt, 33·5 per cent).

The residue on the filter after filtering the hot mixture was washed several times with hot alcohol and hot water to remove the last traces of the compound $PtCl_2 \cdot 4\ C_5H_5N$. It was then washed with alcohol, benzene and ether. The substance is insoluble in common organic solvents. It could not be obtained in a very pure state and contained traces of sulphur, m.p. 261-65° (decomp.). (Found: Cl, 23·46; Pt, 40·2. $PtCl_3 \cdot 2\ C_5H_5N$ requires Cl, 23·1; Pt, 40·3 per cent).

Action of dimethylaniline on $PtCl_3 \cdot C_6H_{14}S_2$.—$PtCl_3 \cdot C_6H_{14}S_2$ was treated with a slight excess of dimethylaniline in a hard glass test tube and heated on a water-bath for 2 to 3 hours with occasional stirring. A deep violet solution was obtained which was filtered and to the filtrate excess of an ether-alcohol mixture (1:1) was added, when a precipitate was found to separate. The precipitate thus obtained was dissolved in acetone and reprecipitated with ether. It was then collected and washed several times with alcohol and finally with ether and dried in vacuum. It is a very light greenish substance, m.p. 187°. (Found: Cl, 16·92; S, 15·36; Pt, 47·1. $PtCl_2 \cdot C_6H_{14}S_2$ requires Cl, 17·06; S, 15·40; Pt, 46·87 per cent).

Action of ethylenediamine on $PtCl_2 \cdot C_6H_{14}S_2$.—Ethylenediamine (5 c.c.) was added to $PtCl_2 \cdot C_6H_{14}S_2$ (5 g.) in aqueous suspension (20 c.c. water). After keeping the mixture in a closed flask for a day, whole of $PtCl_2 \cdot C_6H_{14}S_2$ went into solution with the liberation of the disulphide which is removed from the mixture by extracting with ether. The aqueous extract on concentration in vacuum over sulphuric acid gave light brownish crystals, m.p. 308° (decomp.) [Found: Pt, 50·32. $PtCl_2 \cdot 2C_2H_4(NH_2)_2$ requires Pt, 50·51 per cent].

Action of pyridine on $PtCl_2\ C_6H_{14}S_2$.—To $PtCl_2 \cdot C_6H_{14}S_2$ a quantity of pyridine just sufficient to dissolve the substance was added, the solution was diluted with alcohol and allowed to stand for 3 days in a loosely stoppered flask, when a crop of fine white

crystals was found to separate and collected as usual. The substance is soluble in water, becomes yellow at 120°, and melts at 285°, (decomp.). (Found: Pt, 33·41. $PtCl_2 \cdot 4\ Py$ requires Pt, 33·5 per cent).

Preparation of the compound $PtCl_4 \cdot C_6H_{14}S_2$.—$PtCl_3 \cdot C_6H_{14}S_2$ (10 g.) was well triturated with water (120 c.c.) and to this mixture fuming hydrochloric acid (50 c.c.) was added, followed by perhydrol (30 c.c.) with stirring. The mixture was allowed to stand for 2 days in a loosely stoppered flask. The insoluble residue was then collected and washed as usual. The substance is light orange-coloured and insoluble in ordinary solvents and melts at 230° (decomp.). The substance on further treatment with the mixture of fuming hydrochloric acid and perhydrol was found to melt at the same temperature. (Found: Cl, 29·48; S, 12·91; Pt, 39·86. $PtCl_4 \cdot C_6H_{14}S_2$ requires Cl, 29·16; S, 13·14; Pt, 40·04 per cent).

Action of ethylenediamine on $PtCl_4 \cdot C_6H_{14}S_2$.—$PtCl_4 \cdot C_6H_{14}S_2$ (3 g.) in aqueous suspension (20 c.c. water) was treated with ethylenediamine hydrate in excess. After allowing the mixture to stand in a closed flask for 3 days, whole of $Pt\ Cl_4 \cdot C_6H_{14}S_2$ went into solution with the liberation of the disulphide which was removed by extracting with ether. The aqueous extract was then concentrated in vacuum over sulphuric acid to a small volume and precipitated with alcohol. The first crop of the precipitate was redissolved in a small amount of water and reprecipitated with alcohol. It was finally crystallised from rectified spirit. This is necessary to free the substance from the hydrochloride of the base that might be formed in the reaction. The substance is brownish in colour and melts at 308° (decomp.). (Found: N, 14·32; Cl, 18·5; Pt, 50·6· $PtCl_2$-$2\ C_2H_4\ (NH_2)_2$ requires N, 14·51; Cl, 18·39; Pt, 50·51 per cent).

The ionisability of $PtCl_2 \cdot En_2$ *(Precipitation method)*.—The substance was dissolved in water and $AgNO_3$ solution added in the cold without adding nitric acid. The result obtained is slightly low. [Found: Cl, 17·89. $PtCl_2 \cdot En_2$ (assuming both Cl_2 atoms ionisable) requires Cl, 18·39 per cent).

Action of ammonia on $Pt\ Cl_4 \cdot C_6H_{14}S_2$.—$PtCl_4 \cdot C_6H_{14}S_2$ (5 g.) was covered with liquor ammonia (25 c.c.) and the mixture was kept in a stoppered flask with occasional shaking. After 2 days, whole of the $PtCl_4 \cdot C_6H_{14}S_2$ went into solution with the liberation of the disulphide which was removed by extracting with ether. The aqueous extract was concentrated to a small volume in vacuum and

precipitated with alcohol. The precipitate was collected and the process of solution in water and precipitation with alcohol was repeated twice. The substance is light brownish and very hygroscopic. (Found: Cl, 21·17; Pt, 58·15. $PtCl_2{\cdot}4NH_3$ requires Cl, 21·26; Pt, 58·88 per cent).

Action of pyridine on $PtCl_6{\cdot}C_4H_{14}S_2$.—$PtCl_4{\cdot}C_6H_{14}S_2$ (6 g.) in alcoholic suspension (100 c.c. alcohol) was treated with pyridine (15 c.c.) and the mixture was refluxed on a water-bath for 12 hours, when the light orange colour of the compound gradually changed into light yellow. The yellow compound was collected and washed as usual, m.p. 270° (decomp.). (Found: N, 5·34; Cl, 34·28; Pt, 39·27. $PtCl_4{\cdot}2Py$ requires N, 5·67; Cl, 28·68; Pt, 39·4 per cent).

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Geometrical Inversion in the Acids Derived from the Coumarins.

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In a paper on the hydroxyquinolylacrylic acids and their derivatives (Dey and Seshadri, *J. Indian Chem. Soc.*, 1927, 4, 189) it was pointed out that there existed a fundamental difference between the behaviour of the *trans* acids and of their esters under the action of heat. The former decomposed into the corresponding styrenes and carbon dioxide, whereas the latter eliminated alcohol to form the original pyrones. What was then considered to be an isolated phenomenon peculiar only to the hydroxyquinolylacrylic acids has since been discovered to be a property common to all members of the coumaric acid series.

It was considered to be of some importance to examine if there was any tendency on the part of any of the coumaric acids to go over into the coumarins when heated, and with this end in view the decomposition of *o*-coumaric acid and its nitro and methoxy derivatives was studied closely. No formation of the coumarins was detected and the styrenes were obtained exclusively.

In contrast with the action of heat, the effect of sunlight on the *trans* acids and their esters is found to be quite similar both being converted into the coumarins. The esters, however, underwent inversion more readily than the acids. The effect of substituents such as a methoxy group and a nitro group in the benzene ring has also been investigated. The latter markedly accelerates the transformation of both the acids and their esters, whereas the former produces just the opposite. Table I gives the percentage conversion of the acids and esters when exposed to bright sunshine in alcoholic solution for different intervals of time,

TABLE I.

Substance.	Time of exposure.	Product.	% Conversion.
o-Coumaric acid	24 hrs.	Coumarin	65
Methyl coumarate	,,	,,	87
Ethyl coumarate	,,	,,	74
4-Methoxycoumaric acid	,,	7-Methoxycoumarin	51
Methyl 4-methoxycoumarate	,,	,,	55
Ethyl ,,	,,	,,	55
5-Nitrocoumaric acid	12	6-Nitrocoumarin	99
Methyl 5-nitrocoumarate	,,	,,	100
Ethyl ,,	,,	,,	99
o-Coumaric acid	6	Coumarin	48
Methyl coumarate	,,	,,	54
4-Methoxycoumaric acid	,,	7-Methoxycoumarin	30
Methyl 4-methoxycoumarate	,,	,,	42
5-Nitrocoumaric acid	,,	6-Nitrocoumarin	80
Methyl 5-nitrocoumarate	,,	,,	90

Table II gives the percentage conversion of the *trans* esters into the coumarins when heated. It will be noticed that the effects of the substituents are similar to those found in the photochemical inversion. The conditions of decomposition by heat are, however, not so easily controllable as in the case of light and it would not be correct to draw conclusions of a quantitative nature from these results.

TABLE II.

Ester decomposed.	Time of heating.	Product.	Yield.
Methyl coumarate	5 min.	Coumarin	45%
Ethyl coumarate	,,	,,	46
Methyl 4-methoxycoumarate	,,	7-Methoxycoumarin	44
Ethyl ,,	,,	,,	41
Methyl 5-nitrocoumarate	2 min.	6-Nitrocoumarin	76
Ethyl ,,	,,	,,	73

Experimental.

o-*Coumaric acid* was prepared from coumarin by the method of Dey and Row (*J. Chem. Soc.*, 1924, **125**, 561) as well as by that of Sen and Chakravarti (*J. Indian Chem. Soc.*, 1930, 7, 247), the former method gave a better yield of the pure acid (20 g. from 20 g. of coumarin), the latter method gave only 3 g. of the acid from 5 g. of coumarin. The yield was, however, raised to 4 g. by adopting the following modification:

The purified mercury complex was boiled with dilute alcohol (50 c.c., 50%) and concentrated hydrochloric acid (10 c.c.) for a few minutes and filtered hot. A second extraction of the residue removed a further small quantity. The combined filtrate was boiled to drive off most of the alcohol and on cooling the solution, *o*-coumaric acid crystallised out.

The methyl and ethyl *esters* of the acid were prepared by two methods: (*a*) by boiling coumarin with a molecular equivalent of sodium alcoholate in absolute methyl or ethyl alcohol for 4 hours (Biilmann, *Annalen*, 1912, **388**, 228) and, (*b*) by boiling coumaric acid with absolute alcohol containing 2% anhydrous hydrogen chloride for 6 hours (Biilmann, *ibid.*, p. 279). When alcohol saturated with hydrogen chloride gas was employed for the esterification, ring-closure of the acid occurred giving rise to free coumarin. The *methyl ester* readily crystallised from benzene, m.p. 137°, yield by the first method 20 g. from 29·2 g. of coumarin, whereas by the second method it was 5 g. from 5 g. of the acid. The *ethyl ester* was easily obtained pure and crystalline by dissolving it in light petroleum in which it was very soluble and pouring the solution into a large volume of ligroin, m.p. 86°, yields were 15·9 g. from 29·2 g. of coumarin and 5 g. from 5 g. of coumaric acid.

5-*Nitrocoumaric acid* was obtained from 6-nitrocoumarin (Morgan, *J. Chem. Soc.*, 1904, **85**, 1233). The sodium sulphite method gave a rather poor yield of the acid (7 g. from 20 g. of nitrocoumarin). Modifications in which the nitrocoumarin was boiled for a shorter time with sodium sulphite or in which lower concentrations of potash were used, did not improve the yield. Though the use of mercuric acetate resulted in a better yield, the product obtained was rather impure and required several crystallisations. When mercuric oxide (Sen and Chakravarti, *loc. cit.*) was employed,

however, the process was quicker and the product was obtained purer and in better yield (4 g. from 5 g. of nitrocoumarin).

The methyl and ethyl esters of the acid could not be made direct from nitrocoumarin by using sodium alcoholate since the reagent attacked the nitro group also. It was, therefore, prepared by esterifying the acid with alcohol containing 2% dry hydrogen chloride. The methyl ester melted at 210° (Dey and Row, *loc. cit.*), yield 4·7 g. from 5 g. of the acid. The ethyl ester crystallised as colourless needles which slowly turned yellow on exposure to air, m.p. 170-72°, yield 3·5 g. from 5 g. of the acid. (Found: N, 6·0. $C_{11}H_{11}O_5N$ requires N, 5·9 per cent).

7-*Hydroxycoumarin* (Umbelliferone) (Pechmann, *Ber.*, 1884, 17, 132) was prepared as follows. Equimolecular quantities of dry resorcinol and malic acid were intimately mixed and heated carefully on a wire-gauze with double their weight of concentrated sulphuric acid (*d* 1·88). The mixture began to froth up in a few minutes with evolution of carbon dioxide and eventually solidified. Heating was continued until the solid just remelted and the reaction was then allowed to complete by itself. When the gas evolution ceased the mixture was again heated and the process was repeated till the liquid became suddenly clear and quite free from gas bubbles. After cooling, the melt was poured into five times its weight of ice-water and the solid was crystallised from methanol (charcoal) as colourless rhombic prisms, m.p. 223-24°, yield 4 g from 13 g. of malic acid and 11 g. of resorcinol. (The success of the method was found to depend mainly on the regulation of the heating which should be stopped precisely at the moment the mixture becomes clear.)

7-*Methoxycoumarin* was obtained from umbelliferone by methylating with dimethyl sulphate in presence of aqueous alkali or in presence of anhydrous potassium carbonate in benzene.

Resorcinol (11 g.) dissolved in caustic soda (10%, 40 c.c.) was treated at 60-70° as usual with dimethylsulphate (12-13 g.) and the mixture was finally heated on the boiling water-bath for ½ hour, the oil taken up with ether, the ether distilled off and the oil distilled in steam. The distillate was extracted with ether and then with 10% aqueous caustic soda. The alkaline solution was acidified, extracted with ether, dried and distilled at 242-43°, yield 7·5 g.

The reaction of monomethylresorcinol with malic acid to produce umbelliferone methylether is more easily controlled and the yield is

almost theoretical. The crude product crystallised from metl (charcoal) as colourless leaflets, m. p 117-18°.

4 *Methoxycoumaric acid* was obtained from 7-methoxycour (*i*) by boiling it with alcoholic potash (Barth and Harzig, *Monat* 1889, **10**, 165) and (*ii*) by treatment with sodium sulphite and a yield 2 g. from 5 g. of the coumarin. The esters of the acid obtained by the same methods as were applied in the case of cour acid. The *methyl ester* crystallised from dilute alcohol as colou needles, m. p. 138°. (Found: C, 62·9 ; H, 5·7. $C_{11}H_{12}O_4$ req C, 63·5; H, 5·8 per cent). The *ethyl ester* crystallised from c methanol, m.p. 109°.

Decomposition of the o-*coumaric acids by heat.*—*o*-Coumaric was heated under conditions employed by Krause (*Ber.*, 1908, **41**, for the preparation of *o*-vinylphenol. The distillate as well a residue in the distilling flask were both examined for the preser coumarin by dissolving them in ether, shaking the solution wit aqueous potash so as to remove vinylphenol and its polymers, d the ether solution and evaporating it to dryness. No residue wa thereby showing that coumarin formation did not take place under these circumstances. The decompositions of the nitro methoxycoumaric acids were very vigorous and uncontrollable g rise to brownish resinous residues having the odour of phenol definite compounds could be isolated.

Action of Heat on the Esters of the Coumaric Acids (trans)

Methyl coumarate (1 g.) was heated carefully for 5 minutes dry test tube over a small flame, the contents being stirred. orange-red liquid turned into a mass of crystals on cooling. It dissolved in ether, the undecomposed ester removed with 2% aqu caustic soda and the ether removed. The colourless crystals found to be identical with coumarin, m.p. 67°, yield 45%. The e ester behaved similarly and produced coumarin in an yield of 46%

Methyl and *ethyl 4-methoxycoumarates* produced 7-meth coumarin, m.p. 117-18°. (yield 44 and 41%). The *esters of 5-r coumaric acid* underwent this change more readily and heating minutes was found to be sufficient. The product of decompos was digested in the cold with 2 % aqueous alkali, filtered and fi crystallised from glacial acetic acid, m.p. 183-85° and was found

identical with 6-nitrocoumarin, yields 76% (from the methyl ester) and 73% (from the ethyl ester).

Action of Sunlight on the trans-*Acids and their Esters.*

o-Coumaric acid and its methyl ester were exposed to bright sunshine for 24 hours in silica tubes and were examined at intervals for m. p. and solubility in sodium carbonate and hydroxide respectively. No change was observed. A solution of 2 g. of the pure acid or the ester in 50 c.c. of ethyl alcohol was placed in a silica flask and exposed to bright sunshine for 24, 12 or 6 hours according to circumstances. The weather conditions were uniformly good.

After exposure, the alcohol was distilled off, the residue taken up in ether, the coumaric acid or its ester removed by 5% sodium bicarbonate (2% bicarbonate in the case of ester), washed with water and the coumaric acid dried over sulphuric acid in a vacuum desiccator for 24 hours and the ether removed, yield in case of *o*-coumaric acid 65% (after 24 hours) and 48% (after 6 hours). Methyl coumarate gave (87% after 24 hours and 54% after 6 hours) coumarin, whereas ethyl coumarate gave coumarin (74% after 24 hours).

4-*Methoxycoumaric acid* was treated just in the same way as coumaric acid. It yielded 0·92 g. of 7-methoxycoumarin after 24 hours' exposure (51%) and 0·60 g. after 6 hours (30%). The methyl ester gave 0·94 g. of methoxycoumarin after 24 hours (55%) and 0·72 g. after 6 hours (42%), whereas the ethyl ester gave 0·87 g. of methoxycoumarin (56%) after 24 hours' exposure.

5-*Nitrocoumaric acid.*—The original orange-red solution of the acid turned paler as the exposure proceeded and needle shaped yellow rystals of 6-nitrocoumarin began to separate. At the end of 6 or 12 hours' exposure (the conversion was found to be complete after 12 hours) the solvent was distilled off and the residue was digested with cold aqueous sodium bicarbonate in order to remove the unchanged acid, filtered, washed with water, dried in a desiccator and weighed. This purification was not necessary after 12 hours' exposure since the residue after removing alcohol was found to be pure nitrocoumarin showing no trace of the presence of the unchanged acid, yield of nitrocoumrin after 12 hours was 1·8 g. (99%) and after 6 hours' exposure 1·5 g. (80%).

The esters also underwent complete conversion after 12 hours' exposure ; the methyl ester gave 1·69 g. and the ethyl ester 1·59 g. of pure 6-nitrocoumarin. After 6 hours' exposure, however, the reaction was still incomplete ; the unchanged ester in the product was removed by digestion with cold 2% aqueous potash, filtered, washed with water, dried and weighed. The yield from the methyl ester was 1·5 g. (90% conversion).

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Kinetics of Sucrose Inversion by Adiabatic Temperature Measurements.

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Variation in the heat content of a reactive system is amon most conspicuous results produced by a chemical change. It be anticipated, therefore, that a parallelism would exist betw progress of a reaction and of the corresponding time variation temperature of the system. In a study on this basis of the] of a change, an adequate thermal insulation of the reactive s and a reckoning of the possible influence of the temperature rate of change would appear to be the chief factors requiring ful consideration. Bredig and Epstein (*Z. anorg. Chem.*, 19 341) appear to have been perhaps the first to recognise the utility of this method, and Barry (*J. Amer. Chem. Soc.*, 1(1911, 1926) to use it in the kinetics of sucrose inversion. felt, however, that need existed for a modified procedure y data both accurate and in a form which can be treated direct a theoretical standpoint. Measurements have been also carri on the specific heat of sucrose solution and the influence of on the heat of dilution of hydrochloric acid by water.

In his work Barry (*loc. cit.*) introduced a known amount (sucrose in the acid of the desired strength kept in the calo The dissolution of sucrose in an acid solution is endothermic effect is partly superimposed upon that due to sucrose inversi temperature of the reaction mixture would, therefore, rise slc the *initial* stages. It was also felt that this would add to th period of disturbance which obtains when even liquids are and which has been ascribed to the slow homogenisation of t tion mixture (*cf.* especially Scatchard, *J. Amer. Chem. Soc.* **48**, 2259 ; also, Lamble and Lewis, *J. Chem. Soc.*, 1914, **10** In the following experiments a definite amount of the acid has been added to a sucrose solution in the calorimeter.] more, unlike Barry, the temperature measurements have be tricted only to the *initial* stages of the inversion so that the ature rise is not appreciable ; this is necessary since the rea known to be sensitive to temperature changes (*vide infra*).

Experimental.

The reaction was carried out in a Dewar flask of about capacity and was enclosed in a heavy copper cylinder leaving

gap of 1 cm. The cylinder and the Dewar flask were fitted respectively with a copper and an ebonite cap, each of which was perforated to admit a Beckmann thermometer, the stem of a small funnel and a perforated, reciprocating gold stirrer, operating vertically. The copper cylinder was placed in a water thermostat of about 90 litres capacity, whose temperature was kept constant at 30° within 0·01°. The Dewar flask contained 250 c.c. of sucrose solution of the desired concentration and was heated electrically to 30° in all the experiments. 50 C c of a solution of hydrochloric acid of known strength preheated to 30° were then added carefully through the funnel to the sucrose solution, and the corresponding time noted. The weight of this solution of the hydrochloric acid added varied in the range, 51·48 to 51 6 g in the various experiments. The temperature of the mixture was then observed within 0·001° at regular intervals by means of a Beckmann thermometer and a special telescope. Figs. 1-4 show the Beckmann readings with time during sucrose inversions by four acid concentrations. The strength of the sucrose solution is expressed in terms of the weight in g. of the solute in 100 c.c. of the reaction mixture at 30° and the stirring of the mixture, which was started before the addition of the acid, was so regulated that there was no sensibie thermal lag in the record of the temperature by the Beckmann thermometer (except curve 4, Fig. 4). Curve 6 in Fig. 6 is a typical curve showing the Beckmann reading during the progress of one inversion AB, the horizontal part of this curve denotes time of constant temperature before this addition of the acid. The sudden rise in BC is due to the dilution of the acid added (*vide infra*). Progress of the inversion is, therefore, represented only by the last section of the curve, CD. In order to economise space and prevent overlapping, these temperature-time readings have been presented graphically in Figs. 1-4, after the addition of a convenient constant to the series of Beckmann readings obtained for any given inversion. In drawing these curves points corresponding to sections AB and BC in curve 6 of Fig. 6 have not been employed. For example, the actual Beckmann readings at different times during inversion of 15 % sucrose solution by 4·92N-HCl are shown graphically by curve 6 in Fig. 6. Curve 4 in Fig. 3 was drawn from this by subtracting 2·125 from the Beckmann readings plotted in the section CD (curve 6, Fig. 6). It is obvious that this procedure does not alter the *time rate* of temperature rise in a given inversion. On the other hand it has the advantage of representing the time-temperature curves characteristic of the inversions of variously

concentrated sucrose solutions in the same figure and with the san co-ordinates. These curves shown in Figs. 1-4 refer to inversions which the acid strength was varied in the range 0·4 to 0·9N, and th of the sugar from about 2 to 80 % by weight of the reaction mixtur From these curves as explained later, the values of k, the velocit coefficients for sugar inversion at various sugar and acid concentr tions have been deduced and the results shown in Tables I-IV.

It will be seen from the typical time-temperature curve 6 of Fi 6 that there is at first a large and a sudden rise of temperatu which is followed by a slower rise. The first temperature rise is du almost entirely to the heat of dilution of the acid and is followed b that due to inversion. The two sections are separated by a appreciable discontinuity in the curve. Moreover, the second sectio begins fairly close to the temperature axis. The temperature ris due to the first factor, *viz.*, acid dilution is obtained easily by th extarpolation of the curve for zero time. Curves 1-4 of Fig. 6 sho the variation of this initial temperature rise for the variously co centrated sugar solutions when mixed with acid solutions of differen strengths as mentioned already. Curve 5 in Fig. 6 shows the rise c temperature produced in equal amounts of sugar solutions in th same range of dilution as above when heated by exactly the sam quantity of electrical energy (*cf.* 7th column, Table V).

It was also thought desirable to measure the specific heats c sugar solutions at different dilutions (*cf.* Table V) and it was don by the electrical method. 1·1610 amp. was allowed to flow 9 minute through about 300 c.c. of the solution. The consequent temperatur rise was about 3°. The radiation correction varied in the range 0·0 to 0·046°. The accuracy of these measurements is shown by th fact that the water equivalent of the calorimeter could be reproduce within 0·6 %. Details regarding the technique of these measure ments will be described in a later communication. Curve 5 in Fig. and (indirectly curve 5 in Fig. 6) relate respectively the specific hea of solutions of sucrose and of invert sugar with the acid concentra tion. Curves 1-4 in Fig. 5 show the values of k, the velocit coefficient calculated for the initial stages of the inversion (*vide infra*) (*cf.* Tables I-IV) for four series of sugar concentrations, the aci strengths being kept constant in a given series. 'm' in Table I-IV denotes the strength of the sucrose solution in g. of the solut per 100 c.c. of the reaction mixture at 30°; 't' and 'T' denot interval in minutes and temperature respectively; 'k' denotes velo city coefficient for sugar inversion.

TABLE I.

HCl conc. $=0{\cdot}807N$.

t.	m. →	2	3	4	5	6	8	10	13
1 min.	$\frac{\Delta T}{\Delta t}$	0·0025/1	0·00325/1	0·0065/1	0·0080/1	0·0110/1	0·0150/1	0·0180/1	0·0425/1
	,,	0·0025	0·00325	0·0065	0·0080	0·0110	0·0150	0·0180	0·0425
	k	0·00125	0·001083	0·001625	0·001600	0·00183	0·00187	0·00180	0·00327
2·5	$\frac{\Delta T}{\Delta t}$	0·0065/2·5	0·0100/2·5	0·0160/2·5	0·0185/2·5	0·0265/2·5	0·0345/2·5	0·0460/2·5	0·1050/2·5
	,,	0·0026	0·0040	0·0064	0·0074	0·0106	0·0138	0·0184	0·0420
	k	0·0013	0·00133	0·0016	0·00148	0·00176	0·001725	0·00184	0·00323
5·0	$\frac{\Delta T}{\Delta t}$	0·0120/5	0·0200/5	0·0320/5	0·0375/5	0·0520/5	0·0690/5	0·09055	0·2150/5
	,,	0·0024	0·0040	0·0064	0·0075	0·01040	0·0138	0·0181	0·0430
	k	0·00120	0·001330	0·001600	0·001500	0·00173	0·00172	0·00181	0·00330
10	$\frac{\Delta T}{\Delta t}$	0·024/10	0·0405/10	0·0610/10	0·0730/10	0·0940/10	0·1365/10	0·1765/10	
	,,	0·0024	0·00405	0·00610	0·00730	0·00940	0·01365	0·01765	
	k	0·00120	0·00135	0·001525	0·00146	0·00156	0·00170	0·001765	
15	$\frac{\Delta T}{\Delta t}$	0·0350/15	0·0560/15	0·0840/15	0·1050/15	0·1340/15	0·1890/15	0·249/15	
	,,	0·00233	0·00373	0·0056	0·0070	0·00893	0·0126	0·0166	
	k	0·001166	0·00124	0·0014	0·0014	0·001486	0·00157	0·00166	
20	$\frac{\Delta T}{\Delta t}$	0·0450/20	0·0690/20	0·1050/20	0·1310/20	0·1720/20	0·2390/20	0·3160/20	
	,,	0·00225	0·00345	0·00525	0·00655	0·0086	0·01195	0·0158	
	k	0·001125	0·00115	0·00131	0·00131	0·00143	0·001493	0·00158	

TABLE II.

HCl conc. = 0·83N.

t	$m.$ →	1	2	4	6	8	10	13
1 min.	$\frac{\Delta T}{\Delta t}$	0·0005/1	0·0020/1	0·0060/1	0·0110/1	0·0180/1	0·0220/1	0·0290/1
,,	,,	0·0005	0·0020	0·0060	0·0110	0·0180	0·0220	0·0290
,,	k	0·0005	0·0010	0·0015	0·00171	0·00225	0·0022	0·00223
2·5	$\frac{\Delta T}{\Delta t}$	0·00015/2·5		0·016/2·5	0·028/2·5	0·043/2·5	0·053/2·5	0·076/2·5
,,	,,	0·0006		0·0064	0·0112	0·0172	0·0212	0·0304
,,	k	0·0006		0·0016	0·00186	0·00215	0·00212	0·002338
5	$\frac{\Delta T}{\Delta t}$	0·003/5	0·004/5	0·0310/5	0·0510/5	0·0880/5	0·1040/5	0·1420/5
,,	,,	0·0006	0·0008	0·0062	0·0102	0·0176	0·0208	0·0284
,,	k	0·0006	0·0004	0·00155	0·00170	0·00220	0·00208	0·00219
10	$\frac{\Delta T}{\Delta t}$	0·005/10		0·0610/10	0·105/10	0·1530/10	0·1850/10	0·2700/10
,,	,,	0·0005		0·00610	0·0105	0·0153	0·0185	0·0270
,,	k	0·0005		0·001525	0·00176	0·00191	0·00185	0·00207
15	$\frac{\Delta T}{\Delta t}$	0·008/15		0·086/15	0·147/15	0·215/15	0·260/15	0·280/15
,,	,,	0·00053		0·00573	0·00980	0·0143	0·0173	0·0186
,,	k	0·00053		0·00143	0·00163	0·00179	0·00173	0·001435
20	$\frac{\Delta T}{\Delta t}$				0·185/20	0·271/20	0·324/20	
,,	,,				0·00925	0·01355	0·0162	
,,	k				0·001541	0·001693	0·00162	

Table III.

HCl conc.$=0·82N$.

t.	m. →	5	10	15	20	25	30
1 min.	$\frac{\Delta T}{\Delta t}$	0·0075/1	0·015/1	0·028/1	0·040/1	0·035/1	0·052/1
,,	,,	0·075	0·015	0·028	0·040	0·035	0·052
,,	k	0 0015	0·0015	0·00186	0·00200	0·0014	0·00173
2·5	$\frac{\Delta T}{\Delta t}$	0·018/2·5	0·035/2·5	0·070/2·5	0·099/2·5	0·091/2·5	0·1275/2·5
,,	,,	0·0072	0·014	0·028	0·0396	0·0364	0·0510
,,	k	0·00145	0·0014	0·00186	0·00198	0·001456	0·0017
5	$\frac{\Delta T}{\Delta t}$	0·035/5	0·070/5	0·140/5	0·195/5	0·180/5	0·260/5
,,	,,	0·007	0·0014	0·028	0·039	0·036	0·052
,,	k	0·0014	0·0014	0·00186	0·00195	0·00144	0·00173
10	$\frac{\Delta T}{\Delta t}$	0·067/10		0·265/10	0·390/10	0·358/10	0·517/10
,,	,,	0·0067		0·0265	0·039	0·0358	0·0517
,,	k	0·00134		0·00176	0·00195	0·00143	0·00172
15	$\frac{\Delta T}{\Delta t}$	0·096/15	0·193/15	0·380/15	0·556/15	0·535/15	0·752/15
,,	,,	0·0064	0·01286	0·0253	0 03706	0·0356	0·05013
,,	k	0·00128	0·001286	0·001686	0·001853	0·001424	0·001671
20	$\frac{\Delta T}{\Delta t}$	0·125/20	0·242/20	0·483/20	0·706/20	0·695/20	0·954/20
,,	,,	0·00625	0·0121	0·02415	0·0353	0·03475	0·0477
,,	k	0·00125	0·00121	0·00161	0·001765	0·00139	0·00159

TABLE IV.

$HCl = 0{\cdot}41N$.

t.	$m. \rightarrow$	5	10	15	20	25
1 min	$\frac{\Delta T}{\Delta t}$	0·004/1	0·006/1	0·009/1	0·013/1	0·020/1
,,	,,	0·004	0·006	0·009	0·013	0·020
,,	k	0·00080	0·00060	0·00060	0·00065	0·00080
2·5	$\frac{\Delta T}{\Delta t}$	0·0095/2·5	0·0125/2·5	0·021/2·5	0·033/2·5	0·0495/2·5
,,	,,	0·0038	0·0050	0·0084	0·0132	0·0198
,,	k	0·00076	0·00050	0·00056	0·00066	0·000792
5	$\frac{\Delta T}{\Delta t}$	0·019/5	0·026/5	0·043/5	0·066/5	0·100/5
,,	,,	0·0038	0·0052	0·0086	0·0132	0·020
,,	k	0·00076	0·00052	0·00057	0·00066	0·00080
10	$\frac{\Delta T}{\Delta t}$	0·0375/10	0·050/10	0·0845/10	0·133/10	0·198/10
,,	,,	0·00375	0·0050	0·00845	0·0133	0·0198
,,	k	0·00075	0·00050	0·00056	0·00066	0·00079
15	$\frac{\Delta T}{\Delta t}$	0·0545/15	0·0750/15	0·124/15	0·195/15	0·2915/15
,,	,,	0·00363	0·005	0·00826	0·0130	0·01941
,,	k	0·000726	0·00050	0·0005507	0·00065	0·0007765
20	$\frac{\Delta T}{\Delta t}$	0·070/20	0·098/20	0·163/20	0·258/20	0·379/20
,,	,,	0·0035	0·0049	0·00815	0·0129	0·01895
,,	k	0·00070	0·00049	0·000543	0·000645	0·000758

TABLE V.

Vol. of the sucrose soln. 300 ± ·05 c.c. (50°). P.D. across the heating coils = 6·8250 volts. Current passed = 1·1610 amps. during 540 sec.

Sucrose soln.	Comp. and wt. of soln. Sucrose	+	Water	=	Soln.	Initial temp.	Final temp.	Temp. rise.	Sp. heat.
0%	0·0g.	+	298·6g.	=	298·6g.	2·225	5·318	3·088	0·9987
2	6·0	+	294·4	=	300·4	2·120	5·215	3·095	0·9860
4	12·0	+	289·6	=	301·6	2·190	5·314	3·124	0·9716
8	24·0	+	283·5	=	307·5	2·284	5·424	3·140	0·9479
13	39·0	+	274·4	=	313·4	2·240	5·579	3·159	0·9289
	Invert sugar								
10·5	31·6 g	+	272·1 g.	=	303·7g.	1·960	5·192	3·232	0·9335
					(309·9)	—	—	(3·1672)	—
21·1	63·2	+	254·0	=	317·2	2·004	5·192	3·188	0·9074
31·6	94·7	+	223·5	=	318·2	1·870	5·098	3·228	0·8921

DISCUSSION.

It is seen from the curves in Figs. 1-4 (in which the *initial* temperature rise due to the dilution of the acid is not shown), with the exception of curve 3 in Fig 2 and curve 4 of Fig. 4, that the progress of inversion is accompanied by a continuous rise of temperature as a result of the accumulation of the heat due to the change in the reaction vessel (which is thermally insulated from the environment, *viz.*, the thermostat kept at a constant temperature). This temperature rise over the initial temperature in the reaction vessel varied in the range 0·006° to 0·42° (*cf.* curves 2 and 7 in Fig. 2 and 3 respectively). The observed time-temperature curves are, therefore, subject to but negligible correction in respect of the influence of the temperature on the rate of sucrose inversion. Furthermore, these

observations were taken during about 20-25 minutes from the commencement of the change. They represent, therefore, but the initial stages of the reaction.

It is interesting to note from the curves in Figs. 1-4 that the time-rate of the temperature rise due to sucrose inversion increases by increasing the sucrose concentration, if the acid concentration is kept constant. Similiar to this is the influence of varying the acid concentration, that of sucrose being kept constant. This last is to be anticipated in view of the well known influence of the acid concentration on the inversion rate, which determines the rate of the temperature rise produced in the system during the reaction.

It is to be noted from curve 5 in Fig. 6, showing the temperature rise when a fixed quantity of heat produced electrically was dissipated in a constant weight of variously concentrated solutions of sucrose and of invert sugar, that the specific heats for the latter (*cf.* p', q and r, in the above curve) can be represented fairly well on the specific heat-concentration curve for sucrose, *viz.*, curve 5 in Fig. 6. This together with the data recorded in Table V shows that the heat capacity of sucrose solution does not change appreciably due to inversion. Since the acid concentration remains constant during inversion and that the maximum rise in temerature produced is about 0·32° only (during about 25 minutes), it has been assumed during the subsequent discussion that C_v, the heat capacity at constant volume of the reaction mixture remains constant during inversion.

Following the usual notation and denoting by Δq, the heat evolved corresponding to Δx, the amount of sucrose inverted.

$$\frac{\Delta x}{\Delta t} = k' (a-x) \qquad \ldots \qquad \ldots \qquad \ldots \qquad (i)$$

$$= k'. \frac{\Delta q}{\Delta t} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (ii)$$

$$= k'. C_v. \frac{\Delta T}{\Delta t} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (iii)$$

$$= k''. \frac{\Delta T}{\Delta t} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (iv)$$

At *initial* stages when to first approximation x is negligible compared with a, we get from (i) and (iv),

$$k=\frac{1}{a}.\frac{\Delta T}{\Delta t} \quad \ldots \quad \ldots \quad \ldots \quad (v)$$

where k is a measure of velocity constant. The values for the quantity $\Delta T/\Delta t$ have been obtained from the t-T curves in Figs. 1-4. The velocity coefficient k is then obtained simply from (v). On examining the k values in Tables I-IV it is seen that during any given inversion, k diminishes with time which is to be anticipated from the approximation introduced in neglecting x compared with a during the early stages of the change. At early stages, however, the values of the velocity coefficient are fairly concordant. This warrants, therefore, to a considerable extent the chief assumption made earlier, especially as regards C_v.

The k values used in drawing curves 1-4 in Fig. 5 have been calculated from data obtained only for the initial stages of the inversions for reasons indicated above. It is seen that except in curve 4 of Fig. 5 corresponding to the smallest acid concentration, k increases considerably with the increase of the initial sucrose concentration. In the familiar mass law expression,

$$\frac{dx}{dt}=k_{v\,i}\,[\text{water}]\times[\text{sucrose}]$$

since the inversion produces ordinarily but negligible variations in the amount of water present, it is considered to be unimolecular. The $k_{vi}\times[\text{water}]$ is, therefore, practically constant, and equals the ordinary velocity coefficient k. Since k_{vi} is constant, and the proportion of water diminishes by increasing that of sucrose in a given mass of solution, it follows that k should diminish, which is contrary to experience. The possible variation of the active mass of water operating but *hydrolytically* according to the above equation can not, therefore, account for the observed increase of k by increasing the sucrose concentration at constant acid strength. Similar results have been obtained by numerous workers (*cf.* Cohen, *Z. physikal. Chem.*, 1897, **23**, 442; Joneg and Lewis, *J. Chem. Soc.*, 1920, **117**, 1120; Moron and Lewis, *ibid.*, 1922, **121**, 1613; Cotton and Chandun, *compt. rend.*, 1924, **179**, 1607; 1926, **182**, 775; 1926, **183**, 1215) and have been ascribed to an increase in the thermodynamic activity of the H ions. Change of k as observed has been also attributed by some workers to the

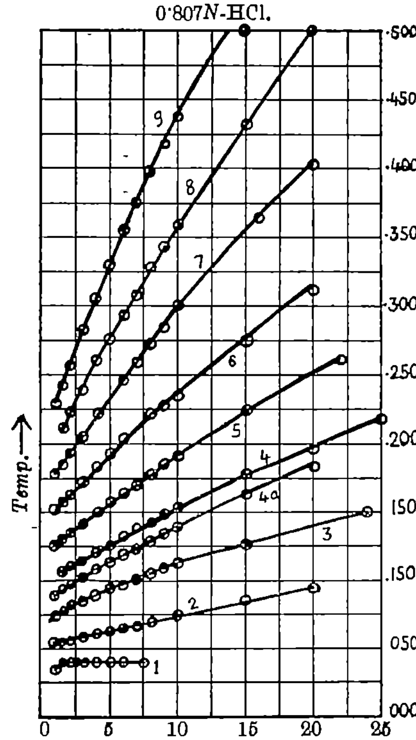
the reduced formation of the unstable sucrose-water com
(which break up into dextrose and laevulose at a rate propor
to the concentration of the complexes) as a result of the di
tion of the water constant (Cotton and Chandun, *loc.*
That the influence of the last factor might be apprecia
indicated by the data in column 3, Table V showing the a
of water present in the various solutions of sucrose used. \
therefore in agreement with this, the results in Table I-III
curves 1-9 in Fig. 5 showing the increase in k by increasin
sucrose concentration are to be anticipated, it is interesting to
from our results that this increase in k appears to be a functi
the acid concentration.

It has been mentioned already that immediately on mixing to
the solutions of sucrose and of the acid, a rapid rise of tempe
(BC, in curve 6, Fig 6) was produced due to the evolution
dilution heat of the acid. This temperature rise varied in the
0·86° to 0·09° (*cf.* curves 1 to 4 in Fig. 6). It is seen
these curves that the *initial* temperature rise diminishes
sucrose concentration is increased. It might be recalled that th
concentration is kept constant in each series. The diminuti
the *initial* temperatare rise with increase of the sucrose concent
in a series might, therefore, be ascribed to (*a*) increase in the
capacity of the solution with the increasing concentration o
solute, (*b*) diminution in the dilution of heat of the acid due to
presence of sucrose, (*c*) increase of the heat of dilution of su
solution, which is known to be negative (*cf.* Vallender
Perman, *Trans. Faraday Soc.*, 1931, **27**, 133) by increasin
concentration of the solution. From considerations indicated al
and data presented in Table V, showing that the specific
of the sucrose solution diminishes by increasing its concentr
it is seen that factor (*a*) is not the operative factor. From the
of Vallender and Perman (*loc. cit.*), Stackelberg (*Z. phy
Chem.*, 1898, **26**, 533), Ewan (*ibid.*, 1894, **14**, 409), Porter (*T
Faraday Soc.*, 1917, **13**, 123) and Hunter (*ibid.*, 1926, **22**, 1
would appear that the order of magnitude for the temper
change due to the negative heat of the dilution of even the
concentrated sucrose solutions employed in these experimen
0·001°, which is negligible compared with the *initial* temper
rise measured (*cf.* curves 1 to 4 in Fig. 6), *viz.*, 0·86-0·09°. I
measurements made with sucrose solutions in the concentr

range of 1-6% of sucrose showed that the fall of temperature due to the heat of dilution was but insensible. The factor (c) would appear, therefore, to be insufficient to explain the effect mentioned above. It is considered, therefore, that (b) represents its most probable cause In this connection it might be pointed out that the temperatnre rise due to the dilution of 50 c.c. of 4·92, 4·84, and 5 N-HCl solutions by 250 c.c. of water was found to be greater than that observed when any of the sucrose solutions was employed (*cf.* curves 1-4 in Fig. 6; also Table V) instead of water. From a knowledge of the mass of a solution and of the corresponding amount of sucrose, A, the amount of the water present in the solution is known (*cf.* column 8, Table V).

FIG. 1.

0·807N-HCl.

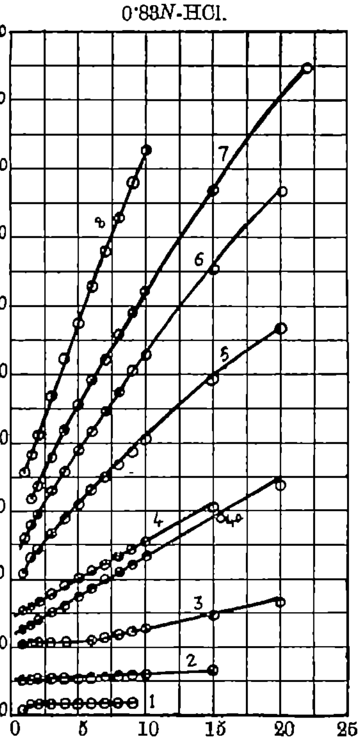


Time in min.

Curves 1 to 9 refer to 0, 2, 3, 4, 5, 6, 8, 10 and 13 % of sucrose solution respectively.

FIG. 2.

0·83N-HCl.



Time in min.

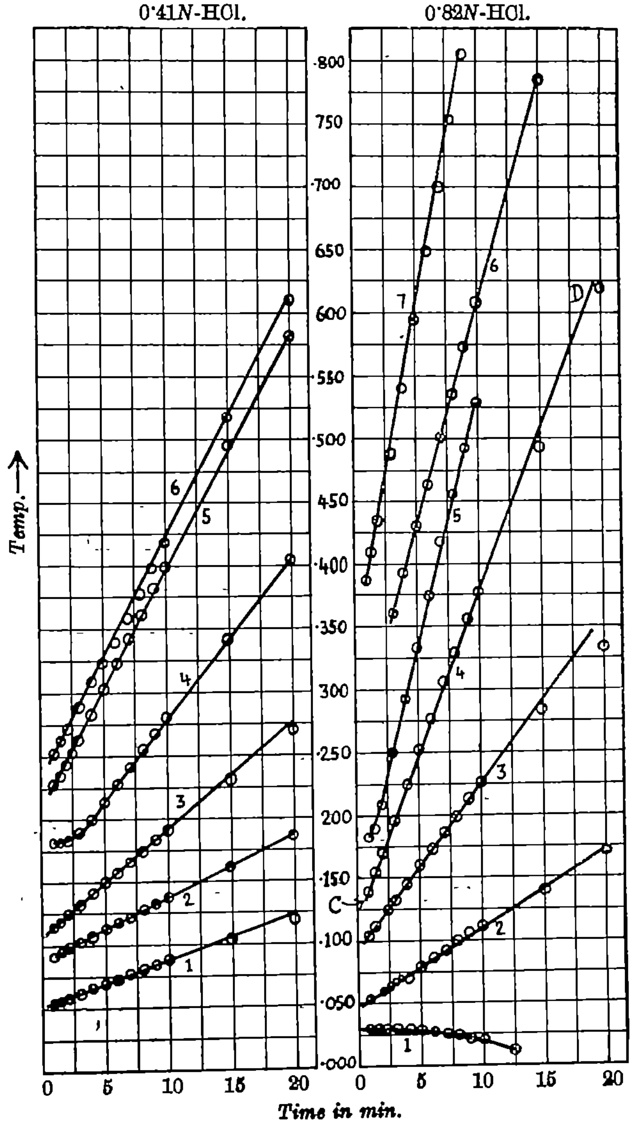
Curves 1 to 8 refer to 0, 1, 2, 4, 6, 8, 10 and 13 % of sucrose solution respectively.

Now general considerations and some actual observations carried out with 5N-HCl solution diluted with volumes of water

in the range, 200-300 c.c. show that the corresponding temperature rise is proportional to the amount of water used in the process of

FIG. 4. FIG. 8.

0·41N-HCl. 0·82N-HCl.

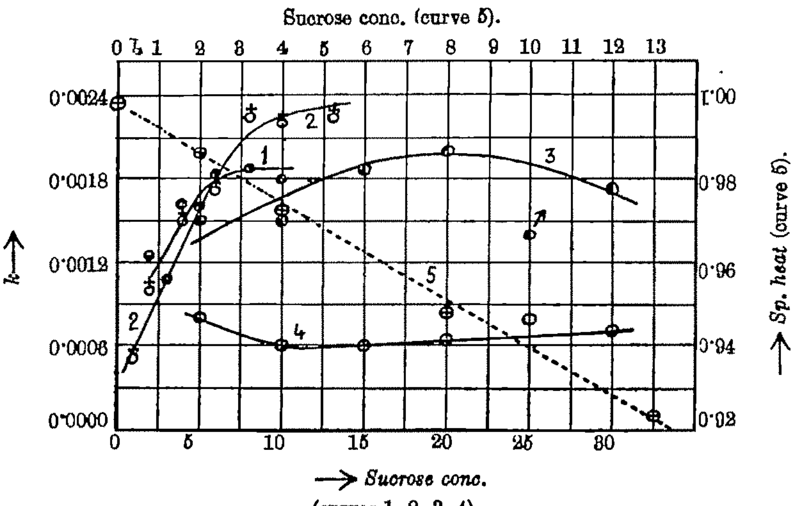


Curves 1 to 6 refer to 5, 10, 15, 20, 25, and 30 % of sucrose soln. respectively.

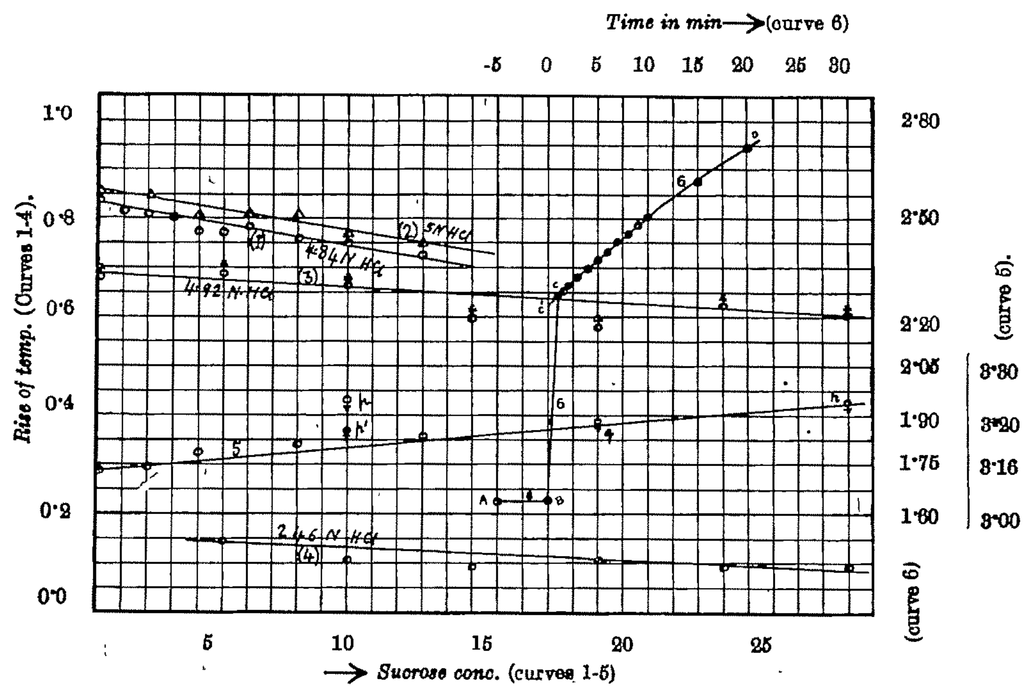
Curves 1 to 7 refer to 0, 5, 10, 15, 20, 25 and 30% of sucrose soln. respectively. Curve 4 of Fig. 8 obtained from specimen curve 6 of Fig. 6.

dilution. The amount of water thus calculated from the values of the *initial* temperature rise (*cf.* curves 1-4 in Fig. 6) was found to be appreciably less than A, in by far the majority of cases. This shows therefore, that a certain amount of water in the solution is not involved in the process of the acid dilution. Presumably therefore, it is bound up in the *hydration* of sucrose in the solution. Results of the detailed investigation carried out to examine this possibility will be communicated shortly.

FIG. 5.



Curve 1 refers to Table I, Fig. 1.
Curves 2-4 refer to Table II-IV and Fig. 2-4 respectively.
Curve 5 shows the variation of sp. heat (scale on the right) with change of sucrose conc. = *m* (scale on the top).



Curves 1-4—Initial rise in temp. due to dilution of HCl by sucrose soln.

Curve 5—Temp. rise due to a constant current passed in equal vol. of differntly concentrated sucrose soln. ; points *p*, *q* and *r* refer to solns. of invert sugar together with the acid used (for other data *cf.* Table V and also curve 5, Fig. 5).

Curve 6—Shows the Beckmann temp. before and during inversion (*cf.* curve no 4 of Fig. 3.). The quantity BC′ obtained by extrapolation of DC in curve 6, gives the initial rise of temp. plotted in curves 1-4, mentioned above.

Summary.

1. Results are given for the temperature rise measured adiabatically during the initial stages of the inversion of sucrose solutions containing 2 to 80 g. of the solute in 100 c.c. of the reaction mixture by 0·4 to 0·9*N*-HCl. An equation is deduced to give *k*, the velocity coefficient from these time-temperature curves. *k* tends to increase by increasing the sucrose concentration if that of the acid is kept constant. This result has been shown to be contrary to the requirements of the law of mass action if the rôle of water be assumed to be merely hydrolytic. This change of *k* with sucrose concentration has been found to depend upon the acid concentration.

2. The specific heats of sucrose solutions have been determined in the range mentioned above. This quantity is found to diminish regularly by increasing the strength of the solution.

3. The heat of dilution of hydrochloric acid solutions has been found to diminish when sucrose solutions are used instead of water, which has been ascribed to the removal of some water from the solvent phase in the hydration of the solute.

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Magnetic Rotation of Some Salts of Higher Fatty Acids and Evidence in Favour of the Formation of Ionic Micelle.

By S. S. Bhatnagar and Pyara Lal Kapur.

Magnetic rotation of the plane of polarisation of various substances like other physical properties, such as electrical conductivity, osmotic pressure, refractive index, surface tension, viscosity, etc., has been extensively studied by Perkin and various other workers. From the measurements, already published, it can be seen that the rotation of salts in solutions is approximately determined additively as the sum of the ions present, if a single substance be present, and is the sum of the components, if more than one substance is there. But there are cases like $FeCl_3$ in water where magnetic rotation varies with concentration (Becquerel, "Smithsonian Physical Tables," 1908, p. 289; Richards and Roberts, *Phil. Mag.*, 1927, **3**, 770) or with temperature (Pillai, *Indian J. Phys.*, 1932, **6**, 578). This is attributed by some to the presence of colloidal Fe_2O_3 particles and by others to the ionisation. In order to decide, therefore, which factor is responsible for this deviation, a study of various sols such as Fe_2O_3, V_2O_5, SiO_2, etc., was undertaken but as the technique of the formation of stable concentrated sols of sufficient transparency is yet not quite perfect, the results obtained will be discussed later. But a study of magnetic rotation of soap solutions which contain colloidal particles, ionic micelle, etc., and are known as colloidal electrolytes has been quite accurately carried out and forms the subiect of the present investigation. So far the magnetic rotations of sodium oleate and potassium oleate solutions in water and alcohol at different concentrations have been studied.

Experimental.

The salts were prepared in the laboratory by the method advocated by McBain. Alcoholic solution of sodium or potassium hydroxide was added gradually to an alcoholic solution of oleic acid and the neutrality of the mixture was tested by phenolphthalein. The soap was then dried first in an oven maintained at 80° and then in a vacuum desiccator till it was completely free from alcohol.

There are two methods generally employed to investigate the magnetic rotation of the plane of polarisation of different substances. One, used by Perkin consists in placing the substances to be investigated between the pole pieces of an electromagnet. The other method which has been extensively employed in the latter work consists in placing an ordinary polarimeter tube inside a large solenoid. It is the latter method that has been adopted in the present investigation because it gives a sufficient length of the liquid column which is desirable for accurate observation of optical rotations.

The solenoid employed was wound over a "former" of a thin fibre tube, 20 cm. long. This consisted of 44 layers each having sixty-seven turns of No. 14 S.W.G., D.C.C. copper wire. The solenoid was nearly 20 cm. long. The internal diameter of the fibre tube was 8 cm.

The current for the solenoid was obtained from the supply of the mains and was capable of fine adjustment by a silding rheostat in series with another variable resistance. A Weston precision ammeter was included in the circuit as well. To obtain fairly large rotation angles for measurement, a current of 9·5 amps. was used which corresponds to effects of 992 watts. This naturally caused a rapid heating of the solenoid.

In view of the dependence of rotation on temperature, it is necessary that some arrangement must be made to take the observations at a constant temperature. The polarisation tube used was, therefore, a double jacketed one. Through the outer jacket water was continuously circulated to keep the temperature of the solution constant.

A Hilger polarimeter with Lippich tripartite field was used. This polarimeter ordinarily is provided with a V-shaped carrier for placing observation tubes. This had to be removed and replaced by a suitable board on which was fixed the large solenoid. The source of light used was a glass mercury vapour lamp with a dichromate filter.

In order to calculate the molecular rotation of a dissolved substance from the measured rotation of the solution, it is assumed that the dissolved substance and the solvent act independently of each other, and that the measured rotation is composed additively from the rotation of these two. This assumption leads, therefore, to the following expression for the molecular rotation of the dissolved substance (with molecular rotation of water as 1) when the dissolving medium is water:

$$M = \frac{D_2}{D_1}\frac{(\mu m_1 + m_2)}{d\, m_1} - \mu \times M_w$$

where M = molecular rotation of the dissolved substance ;

M_w = ,, ,, of the solvent (water = 1) ;

D_2 = measured angle of rotation for solution
D_1 = measured angle of rotation for water
} with the same layer of thickness, temperature and magnetic field.

m_1 = molecular weight of water ;

m_2 = molecular weight of dissolved substance ;

μ = the number of gram molecules of solvent per gram molecule of the dissolved substance ;

d = density of the solution.

It is to be expected that if the assumption mentioned above does not hold, the molecular rotation will vary with concentration.

When the solvent is not water but alcohol, then firstly the molecular rotation of alcohol is determined by the following expression:

$$m_S = \frac{\gamma_1}{\gamma} \times \frac{M}{d \times m}$$

where γ_1 = rotation of solvent, γ = rotation of water, M = molecular weight of the solvent, m = molecular weight of water, d = density of the solvent, and then the molecular rotation of the solution is calculated by Otto Humbug's formula (*Z. physikal. Chem.*, 1893, 12, 402),

$$d_m = \frac{w \times M_1 \times 100}{w_{H_2O} \times S \times 18 \times a}$$

where w = rotation of solution, w_{H_2O} = rotation of water, S = density, a = % of the substance present in the solution, M_1 = molecular weight of the solute, M, the molecular rotation of the dissolved substance is then $d_m = m_s$

where d_m is the molecular rotation of the solution and m_s is the molecular rotation of the solvent.

The results obtained are tabulated below.

TABLE I.

Magnetic rotation of sodium oleate in water.

Solution.	m_2.	a.	μ.	d.	D_2/D_1.	M.
A	304·25	18·02	77·0	1·0027	1·054	21·8
B	,,	13·39	109·4	0·9997	1·033	21·1
C	,,	10·89	138·3	0·9995	1·024	20·6
D	,,	7·09	221·4	0·9981	1·014	20·5
E	,,	5·76	276·6	0·9976	1·017	22·6
F	,,	2·96	553·3	0·9966	1·005	21·6

TABLE II.

Magnetic rotation of potassium oleate in water.

Solution.	m_2	a.	μ.	d.	D_2/D_1.	M.
A	320·37	13·84	110·8	1·002	1·042	22·4
B	,,	11·90	131·8	1·001	1·029	22·6
C	,,	7·723	212·7	1·000	1·026	23·6
D	,,	5·16	326·6	0·9977	1·019	25·2
E	,,	3·24	531·4	0·9960	1·013	27·2

TABLE III.

Magnetic rotation of potassium oleate in alcohol.

Molecular rotation of alcohol = 2·283.

Solution.	M_1.	a.	μ.	S.	w/w_{H_2O}.	M.
A	320·37	19·35	20·02	0·8333	0·9348	20·47
B	,,	18·57	30·54	0·8309	0·9249	20·50
C	,,	16·40	35·50	0·8283	0·9241	20·90
D	,,	15·01	39·52	0·8247	0·9200	20·70

The % column (a) gives the solution's percentage contents of the stated substances.

DISCUSSION AND SUMMARY.

From the tables it is clear that the magnetic rotation both in the case of potassium and sodium oleates in water varies with concentration and has a maximum value at a concentration of 5·70% in the case of sodium oleate and at 3·2% in the case of potassium oleate. In case of potassium oleate in alcohol, the magnetic rotation is practically canstant and the value is 20·67±0·2.

It has been shown by various workers that the magnetic rotation of various substances in non-ionising media remains constant, but in ionising media great anomalies are exhibited. In some the rotation increases with dilution, in others it decreases with dilution, whereas there are a few in which it remains constant.

The magnetic rotation of potassium oleate in alcohol at different concentrations remains almost constant. It can be assumed, therefore, that potassium oleate does not ionise in alcohol. But as magnetic rotation of aqueous solutions of potassium and sodium oleates varies with concentration it indicates that solute and solvent do not behave independent of each other.

It is well known that at low concentrations these salts behave as crystalloids and as the solutions become concentrated the ions coalesce to form the nucleus of colloidal particles, termed the ionic micelle, which have general formula $(Col)_{\chi}\ (ol)_{n}^{(n)^{1}}\ (H_2O)_m$. The amount of water of hydration is least in concentrated solutions.

From Table I, it can be seen that in case of sodium oleate, with the increase of concentration the rotation goes on increasing till the concentration acquires a value of 5·76%. After this the rotation begins to fall till a concentration of 10 89% is reached and then it remains practically constant. These variations indicate that soap solutions belong to that class of compounds in which the rotation decreases with dilution.

The whole behaviour can be explained by assuming that in these cases the rotation goes on increasing with the increase of concentration and at the same time ionic micelle are formed which have a lower rotation value. At a concentration of 5·76% the different phases are in equilibrium and after that the concentration of ionic micelle increases with the result that the rotation goes on falling till it reaches a value of 10·89%. Beyond this there are only ionic micelle in the solution. Therefore the rotation value is practically constant.

These results are in accord with the results obtained by McBain, Laing and Titley (*J. Chem. Soc.*, 1919, **115**, 1279) by a study of changes of electrical conductivity with concentration of these salts. They found the electrical conductivity to be minimum at the concentration where the rotation obtained by us is maximum and to be maximum where the rotation is minimum.

Further work on other allied salts is in progress and the results will be communicated later on.

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A Colorimetric Test for Compounds Containing CH, CH_2 and CH_3 Contiguous to Negative Groups: A Note.

By M. Goswami, A. Shaha and B. Mukerjee.

In some experiments for the detection of oil soluble proteins, acetone solution of the fat was tested with an alkaline solution of picric acid; an instantaneous red coloration was produced. Blank experiment showed that the coloration was due to acetone. The test was then extended to other ketones and then to aldehydes. It was found that all aldehydes and ketones having contiguous CH, CH_2 or CH_3 groupings gave similar red coloration whereas other aldehydes and ketones like formaldehyde, benzaldehyde and benzophenone in which the above groupings are absent, did not produce any colour. Similar observations have been previously made by Bitto (*Annalen*, 1892, **269**, 377, 1892, **267**, 372) who found that *m*-dinitrobenzene, *m*-dinitrotoluene, *m*-dinitronaphthalene and sodium nitroprusside in alkaline media produce red to violet colour with aldehydes and ketones having CH_2 or CH_3 contiguous to CHO or CO groups.

In searching for the reason for such coloration it was thought that the latter was due to the activity of CH, CH_2 and CH_3 being in proximity to the negative groups CHO and CO. The correctness of this view would naturally lead to the production of colour with other compounds containing those active units attached to other negative groups like NO_2, CN, CO_2Et etc. This has been found to be the case as nitromethane, malonic ester, cyanoacetic ester, etc., give red colour with alkaline picric acid solution. All varieties of compounds have been examined and the test has been found to respond very satisfactorily. Generally it has been found that the production of colour always happens when the contiguous negative groups contain oxygen atom and is particularly associated with compounds containing CH_2 or CH_3 responding to Claisen's condensation reaction.

For the purpose of the colorimetric test a 0·05% alcoholic solution of picric acid (1 c.c.) was taken to which approximately 2*N*-caustic soda solution (2 drops) was added and to the faintly yellow solution, thus produced, a slight quantity of the substance to be tested was added. In the case of insoluble substance a little more alcohol was used. Table I gives the results obtained by the reagent whilst some of the results with Bitto's reagents are shown for comparison in Table II. It may be seen that while picric acid reaction is general Bitto's reagents fail in many cases.

TABLE I.

Reagent used—alkaline soln. of picric acid (faint yellow colour).

Compounds tested.	Colour produced.
Formaldehyde	No change.
Benzaldehyde	,,
Benzophenone	,,
Benzil	,,
Benzoin	,,
Acetaldehyde	Red
Phenylacetaldehyde	,,
Acetone	,,
Acetophenone	,,
Acrolein	,,
Cinnamic aldehyde	,,
Citral	Brown
Benzylacetone	Red
*cyclo*Hexanone	,,
o-Methyl*cyclo*hexanone	,,
m-Methyl*cyclo*hexanone	,,
p-Methyl*cyclo*hexanone	,,
Ionone (α)	Red
Nonyl aldehyde	,,
p-Nitrobenzoyl acetophenone	Orange-yellow
p-Tolylbenzoylmethane	Brown
Nitromethane	Red
Malonic ester	,,
Cyanoacetic ester	,,
Oxaloacetic ester	,,
Acetoacetic ester	,,
*2-Methyl-3-ethyl-1 : 4-$\beta\alpha$-naphthapyrone	,,
*7-Nitro-2-methyl-3-*iso*propylchromone	,,
*6-Bromo-2-methyl-3-propylchromone	,,
*6-Chloro-2 :3-dimethylchromone	,,
*7-Nitro-2-methyl-3-propylchromone	,,
*8-Chloro-2-methyl-3-propyl-chromone	,,

* These compounds have been shown to have active CH_3 group (Chakravarti, *J. Indian Chem. Soc.*, 1932, **9**, 28, 31, 389.)

TABLE II.

Compounds.	With *m*-dinitrobenzene.	With 3 :5-dinitrotoluene.	With sodium nitroprusside.
Formaldehyde	No change	Violet	No change
Acetaldehyde	,,	No change	Pink
Phenylacetaldehyde	Violet	Pink	No change
Acetone	,,	Violet	Pink
Acetophenone	,,	,,	,,
Benzophenone	No change	No change	No change
Citral	Violet	Violet	Pink
*cyclo*Hexanone	,,	,,	,,
Nitromethane	,,	Pink	Green
Malonic ester	,,	,,	Pink
Acetoacetic ester	No change	No change	,,
Cyanoacetic ester	Violet	,,	,,

m-Dinitronaphthalene could not be tested as its alkaline solution is itself red.

In conclusion we wish to express our sincerest thanks to Dr. P. B. Sarkar for the active interest he has taken during the progress of the work.

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The Chemistry of Jute-lignin. Part. V. Chlorination of Lignin.

By Pulin Behari Sarkar.

In a former paper (*J. Indian Chem. Soc.*, 1933, **10**, 263) it has been shown by the author that jute-lignin is not essentially different from other lignins, as it gave similar products on potash fusion and that Cross and Bevan's formula cannot explain their formation. The original formula of Cross and Bevan (*J. Chem. Soc.*, 1893, **12**, 104) was arrived at by studying the chloro compound obtained directly from jute. The empirical formula ($C_{19}H_{18}O_9Cl_4$) was assigned to it. Chlorination of jute-fibre was according to these authors a process of simple substitution and they obtained mairogallol and leucogallol on sublimation of chlorolignin.

Since then chlorination of various woods and separated lignins has been studied by many investigators ; the results obtained are, however, far from being concordant. Thus, Heuser and Sieber (*Z. angew. Chem.*, 1913, **26**, 801) by the chlorination of spruce-wood got a product with 22·7% of chlorine; Powell and Whittaker (*J. Chem. Soc.*, 1924, **125**, 357) got from alkali-lignin a chloro compound whose Cl-content was 35·1% and Rassow and Zickmann (*J. pr. Chem.*, 1929, **123**, 217) were able to isolate a chloro compound with 38·22% of chlorine. Strong (*J. Soc. Chem. Ind.*, 1928, **47**, 196T) repeated the experiment of Cross and Bevan and found that besides substitution, considerable oxidation took place when moist chlorine acted on jute-fibre, so that contrary to Cross and Bevan's results the amount of Cl evolved as HCl was twice that combined with lignin. Strong explained the reaction by equations on the basis of Cross and Bevan's formula. While Jonas (*Z. angew. Chem.*, 1921 **34**, 289) and Waenting (*ibid.*, 1928, **41**, 977, 1001) obtained the same derivative under similar conditions; Rassow and Zickmann (*loc. cit.*) were unable to get a homogeneous chloro compound from pine-wood lignin. According to Freudenberg, Belz and Niemann (*Ber.*, 1929, **62**, 1554) when lignin is brominated only substitution takes place, but no addition; on the other hand, Hibbert and Sankey (*Canadian J.*

Research, 1931, 4, 110) found that both addition and substitution took place. From chlorolignin obtained from sources other than jute, no worker could get any product by sublimation. The process of halogenation of lignin, therefore, requires a critical study and the present investigation was undertaken with a view to throw as much light as possible on the problem.

Contrary to the observations of Cross and Bevan (*Cellulose*, 1903, p. 137) it has been found that dry chlorine acts on jute fibre dried at 110° over P_2O_5 under vacuum and a yellow chloro compound was obtained. The presence of moisture facilitated the process to a great extent but even then all the lignin could not be obtained as chloride easily. If the jute was boiled with 1%KOH for one hour and then chlorinated, the reaction was complete in one hour. As the reaction proceeds in the absence of moisture, it cannot be said that the oxidising action of moist chlorine is necessary to disrupt the so-called chemical union between lignin and cellulose. The effect of alkali-boiling appears to be more physical than chemical, as almost all the alkali could be washed off after boiling, the absorption of 1-2%KOH is explained by the fact that part of the acetyl group in pectin is hydrolysed thereby, as will be shown later on. It cannot also be said that the free alkali reduces the acidity of the medium and facilitates chlorination as has been found by Hibbert and Sankey (*loc. cit.*). It is well known that considerable swelling takes place when cellulose matter is treated with alkali. It seems most probable that the boiling alkali merely increases the size of the pores and thereby makes the passage of chlorine into the fibre easier.

In the case of separated lignin, however, it has been found that moisture has absolutely no effect on chlorination. The chlorination of jute-fibre as well as of isolated lignin is attended with liberation of heat. As is to be expected with an exothermic reaction at low temperature more chlorine entered into lignin, the time being the same. When HCl-lignin was chlorinated at 60° for 4 hours the maximum chlorine-content was only 17·6%. This also was the case when chlorination was done with catalysts like iodine, $FeCl_3$ or $SbCl_3$. The influence of light has been found to be nil, it proceeded as rapidly in the dark as in direct sunlight. When lignin was chlorinated in aqueous suspension, a product was obtained which was to some extent soluble in water and had much lower methoxy value. It was also soluble in alcohol, acetone, phenol, acetic acid, etc. But if the medium was CCl_4, the product was no longer soluble in water

and only sparingly soluble in the organic solvents; the percentage of methoxy was, however, considerably higher. This is obviously due to the oxidising action of chlorine in presence of moisture. In all cases of chlorination about 6 to 7% of methoxy was always lost even when lignin was chlorinated in CCl_4 suspension by dry chlorine. When vanillin was similarly chlorinated, chlorovanillin also suffered a loss of 8% of methoxy. Again, when methyl alcohol was the medium the percentage of chlorine in the product was nearly the same but the methoxy rose up; thus methylation also took place besides chlorination. Chloroform and glacial acetic acid behaved in the same way as CCl_4. Working under identical conditions, a chloro compound with the same percentage of Cl was always obtained from lignin as well from jute.

By a comparative study of the chloro derivatives obtained directly from jute and separated lignin, it has been found that the two are identical in many respects: thus, both the reactions are exothermic and take place with evolution of HCl ; both compounds have the same yellow colour, and they are both ash-free ; both dissolve in dilute alkali with a deep brown colour and on precipitation with acids a compound is obtained which has the same low chlorine content, *viz.*, 17·71%. On heating up to 135-40° both of them evolve HCl and turn brown and the resulting compounds have the same chlorine content again, *viz.*, 17·80%. Both are free from furfural-yielding substances and on distillation with 12% HCl or 28% H_2SO_4 both yield formaldehyde. On sublimation, none gives any product. On re-chlorination in glacial acetic acid both give chloro compounds with the same higher chlorine content, *viz.*, 32·7%. Both of them reduce Fehling's solution readily and both give CO_2 when boiled with 12% HCl even in an atmosphere of hydrogen. When distilled with moderately strong NaOH a distillate is obtained from both, which gives iodoform with iodine and alkali.

The presence of double bond in lignin is still a matter of dispute. To explain the formation of rather stable ligno-sulphonic acids, Klason (*Ber.*, 1920, **53**, 705, 1862, 1864) assumed an ethylene linkage in lignin. Hibbert annd Sankey (*loc. cit.*) from the results of bromination concluded that lignin contained an unsaturated side-chain. In their recent formula for lignin, Kürschner and Schramek (*Tech. Chem. Papier-Zellstoff-Fabr.*, 1932, **29**, 35) made provision for an ethylene linkage to show its analogy to coniferin

and account for the formation of acetic acid on hydrolysis and oxidation. Heuser (*Paper Trade J.*, 1930, **88**, 75) also considers the presence of a double bond in lignin very probable. Mehta (*Biochem. J.*, 1925, **19**, 961) even determined the iodine value of lignin as 139. But from the study of absorption spectra Herzog (*Zellstoff u. Papier.*, 1932, **12**, 10) and Hillemer (*Ber.*, 1933, **66**, 1600) conclude that the side-chain in lignin is saturated. Freudenberg and co-workers (*loc. cit.*) considered the bromination as substitution, but they did not present quantitative data. In the present investigation, this question has been decided by estimating the HCl evolved and Cl combined with lignin. In aqueous suspension lignin (separated) like jute itself, was oxidised by chlorine and the ratio, Cl combined to Cl as HCl was found to be considerably higher (about 1:3). In CCl_4 as medium it was found to be very approximately equal to 1. This was independent of time and temperature of chlorination. As the lignin isolated by HCl contains only traces of Cl (which cannot be estimated) it is clear that no HCl addition to any double bond has taken place during isolation. Nor can dry Cl act as an oxidising agent. These results, therefore, prove conclusively that side-chains in lignin are saturated.

In a previous paper it has been shown that the dioxymethylene group is characteristic of lignin and that much of it is lost during careless isolation (*J. Indian Chem. Soc.*, 1934, **11**, 691). Chlorolignin from jute and lignin were purified by dissolving in alcohol and then in acetone and the final product still gave HCHO on distillation with acids. Thus, it cannot be due to any impurity associated with lignin. But the major portion of the $O{\cdot}CH_2{\cdot}O$ group was lost during chlorination as was the case with the methoxy group as well. Cross and Bevan's formula as also all others except the one by Freudenberg (*Ber.*, 1929, **62**, 1814) does not contain this group. The former cannot also explain the reducing action of lignin and its methoxy value.

Chlorolignin has been found to give CO_2 on distillation with 12% HCl according to the method of Nanji, Paton and Ling (*J. Soc. Chem. Ind.*, 1925, **44**, 253T) even when hydrogen was passed instead of air. The percentage is higher than in HCl-lignin; it may be explained by the fact that the negative substitution by chlorine makes the adjacent COOH group more susceptible to hydrolysis. It is interesting to note in this connection that fructose but not glucose was found to give CO_2 in an atmosphere of hydrogen when similarly treated.

As shown in a previous paper, the mol. wt. of lignin must lie near about 830 ; the mechanism of chlorination can be satisfactorily explained on the basis that lignin has a mol. wt. of 816. Under ordinary conditions, 25·8% of Cl means 8 Cl atoms enter the molecule to give $C_xH_{y-8}O_zCl_8$. On being heated to 135-40° or treated with dilute NaOH in the cold, 3 atoms of Cl are lost as HCl to leave behind a compound with 5 Cl atoms in the molecule, *i. e.*. $C_xH_{y-11}Cl_5O_z$ (with 17·7% of Cl) and during chlorination of lignin at 60° or with catalysts the same product results. On re-chlorination, the original compound gives a product with 11 atoms of Cl, *viz.*, $C_xH_{y-11}Cl_{11}O_z$ (with 32·7% of Cl). The methoxy value also can be explained similarly. Two methoxy groups are present in chlorolignin, which means 5·67% of OCH_3 ; while 5·61% has actually been found. This view is supported by the fact that the mol. wt. of chlorolignin with 25·8% of Cl in phenol has been found to be 1080 by cryoscopic method; the theoretical value is 1090. By the boiling point method Waentig (*loc. cit.*) also got a similar figure for chlorolignin from straw. It is too premature to suggest any structural formula for lignin at this stage.

Experimental

Raw jute, freed from adhering impurities and fatty and resinons matter in the usual way, was dried over P_2O_5 under vacuum. Dry chlorine was passed into the gas-washer containing the jute for 10-12 hours. The fibre turned light yellow. Excess of chlorine was removed by passing dry air through the gas-washer and HCl by water. Chlorolignin was extracted with acetone. Cl in the sample was determined by Piria and Schiff's method, which was found to give the same result as Carius method (Found: Cl, 25·78 per cent).

The same sample of jute was moistened with water and chlorinated in the same way for 4 hours. The fibre turned golden yellow and towards the end it bacame much lighter. Purification was done in the same way (Found: Cl, 25·67 per cent).

Purified jute was boiled with 1% KOH for 1 hour and then chlorinated by moist chlorine in the same way. The reaction was complete in 1 hour, prolonged exposure did not increase the percentage of chlorine (Found: Cl, 25·64%; OMe, 5·64%).

2·7587 G. of purified jute was refluxed with 150 c.c. of KOH (equivalent to 282·0 c.c. of 0·882 *N*-HCl) for one hour and the

washings (until neutral) required 275 c.c. of the HCl, whence 1·25% KOH was absorbed by the jute.

Lignin was separated from jute with 42% HCl at 20° for 24 hours and without acid boiling at the end. Reducing sugars were removed by boiling the neutral lignin with water, the light grey product was free from pentosans. It was dried and finely powdered and then sieved through 200 mesh. About 2 g. of this were suspended in about 50 c.c. of CCl_4 in a gas-washer and Cl was passed for 4 hours while it was occasionally shaken. (Found: Cl, 25·88; OMe, 5·55 per cent).

Chlorination at 60° was done by placing the gas-washer with CCl_4 and lignin in a water-bath and passing Cl into the same. Purification was done as usual. Chlorolignin was heated in a glass tube at 140-60° in a glycerine bath until no HCl was found to evolve. The deep brown mass was washed with water until neutral and Cl was estimated in the sample. The results are shown below.

TABLE I.

Medium.	Time.	Temp.	Moist or dry.	Light or dark.	Analysis Cl.	Analysis OMe.
CCl_4	4 hours	0°	Dry	Diffused	25·67%	5·81%
,,	,,	27	Moist	,,	25·88	5·55
,,	,,	,,	Dry	Sun light	25·81	5·64
,,	,,	,,	,,	Dark	25·72	...
,,	,,	28	Dry	Diffused	25·69	...
,,	,,	60	Moist	,,	17·68	6·24
,,	,,	27	Dry	,,	17·80	... with I_2
,,	,,	,,	,,	,,	17·77	... ,, $SbCl_3$
,,	,,	,,	,,	,,	17·81	6·41 ,, $FeCl_3$
Acetic acid	,,	29	Moist	,,	25·90	6·83
,,	1	,,	,,	,,	17·27	...
$CHCl_3$	4	,,	Dry	,,	25·48	5·40
CH_3OH	4	,,	Moist	,,	23·0	13·23
,,	1	,,	,,	,,	17·97	13·19
Water	4	,,	,,	,,	25·31	1·52

CO_2 was estimated by boiling about 0·5 g. of chlorolignin with 100 c.c. of 12% HCl on glycerine-bath and slowly passing the gas with CO_2-free air through an upright condenser to two gas-washers each

containing 100 c.c. of $N/10$-baryta for 4-5 hours. The upernatant liquid (25 c.c.) was titrated next day and CO_2 determined in the usual way.

Formaldehyde was estimated by distilling about 0·3 g. of the substance with 28% H_2SO_4 according to Tollens' method until the distillate gave no test by Schryver's reagent (*Proc. Roy. Soc.*, 1910, **82B**, 226). The filtered liquid was condensed with excess of dimedone dissolved in dilute NaOH and made just acid with acetic acid (Weinberger, *Ind. Eng. Chem. Anal. Ed.*, 1931, **3**, 365). This was kept at 4° for 24 hours after addition of a saturated solution of NaCl, filtered in a glass filter, washed with water until free from chloride, dried at 110° and weighed. The iodometric method gave too high results owing to the fact that it contained a product which gave iodoform under these conditions. The cyanide method could not be employed due to the fact that it contained traces of HCl.

The mol. wt. was determined by the freezing point method in phenolic solution. Care was taken to avoid moisture and not to allow the temperature of the surroundiug bath to rise 2-3° higher than that of the solution, as anomalous results were obtained otherwise. The results are shown in Tables II and III.

TABLE II.

Sample.	Cl.	OMe.	HCHO.	CO_2.	Mol. wt.	Cl in product after NaOH treatment.	Cl in sample after heating to 135-40.	Cl in re-chlorinated product.	OMe in re-chlorinated product.
Cl-lignin from jute	25·64%	5·61%	0·74%	4·20%	1080	17·70%	17·84%	32·74%	4·38%
,, from HCl-lignin	25·88	5·55	0·70	3·94	...	17·78	17·88	32·87	4·41
,, in H_2O	25·31	1·52	...	...	1074	...	...	...	...

TABLE III.

Chlorolignin from jute. *K for phenol=72.*

Substance.	Phenol.	Δ in 0°	Mol. wt.	Mean.
(*i*) 0·2470 g.	19·11 g.	0·085	1095	
(*ii*) 0·1522	22·62	0·045	1067	1080
(*iii*) 0·2015	20·56	0·065	1078	

Chlorolignin from HCl-*lignin in aqueus suspension.*

Substance.	Phenol.	Δ in 0°	Mol. wt.	Mean.
(*i*) 0·2140 g.	20·42 g.	0·070	1077	
(*ii*) 0·1876	22·06	0·055	1113	1074
(*iii*) 0·2206	21·52	0·075	1032	

Ratio of Cl : HCl.—0·3 to 0·4 G. of dry powdered and sieved lignin and 50 c. c. of CCl_4 (dry) were taken in a gas-washer and dry chlorine gas was passed through it very slowly (1 to 2 bubbles per second). This gas-washer was connected to a second washer containing about 100 c. c. of water. The latter was wrapped with a thick black cloth to minimise the formation of HCl. After the reaction, excess of Cl was removed by passing dry air, during which process all the CCl_4 evaporated off. Absence of Cl was tested by starch-iodide paper. In some cases it was necessary to place the gas-washer containing water on boiling water while air was passed through it. The chlorolignin was carefully removed quantitatively, washed with water until neutral, dried and Cl was estimated as before. The washings were added to the gas-washer containing aqueous HCl and total HCl was estimated by titration with $N/10$-alkali in the usual way. As a little HCl was still formed by the action of chlorine on water even when it was covered with black cloth, it was necessary to perform a blank experiment with the same quantity of water and for the same time, and the titre for HCl (about 4 c. c. of N/10-NaOH) deducted from the volume of NaOH. The amount of HCl was always slightly higher than the Cl combined. This is explained by the fact that during removal of chlorolignin, slight traces imperceptively remained on the walls of the gas-washer.

Table IV.

Lignin.	Time.	Temp.	Cl as HCl.	Cl in combination.	Ratio $\frac{Cl}{HCl}$.
0·3029 g.	4 hrs.	28°	0·1506 g.	0·1404 g.	1·07
0·3080	8	28	0 1314	0·1264	1·04
0·2860	1	29	0·1126	0·1006	1·11
0·2575	"	60	0·0865	0·0785	1·10
0·2015	"	60	0·0758	0·0740	1·03

SUMMARY.

1. Dry Cl acts on dry jute to give a chlorolignin with the same percentage of Cl as moist Cl; but the reaction is very slow.

2. The effect of boiling KOH (1 % for 1 hour) on chlorination appears to be more physical than chemical.

3. Light has no influence on chlorination; in presence of catalysts like I_2, $FeCl_3$ or $SbCl_3$ as also at 60° the maximum Cl-content was 17·7 % only.

4. Besides chlorination, methylation takes place when lignin is chlorinated in presence of methyl alcohol.

5. By careful chlorination, the same chloro compound (with 25·8 % of Cl) is always obtained provided the time is 4 hours and lignin is very finely powdered.

6. The percentage of Cl falls down to 17·7 if the chlorolignin is treated with dilute NaOH at room temperature as well as when it is heated to 135-40° for 3-4 hours.

7. By estimating Cl as HCl and that in combination, it has been shown that HCl-lignin contains no double bond.

8. The chlorolignins from jute and separated lignin have been shown to be almost identical.

9. Chlorolignin gives CO_2 even in an atmosphere of hydrogen when boiled with 12% HCl, this is probably due to a COOH group in lignin.

10. The dioxymethylene is partially lost during chlorination as also the methoxy.

11. By acid or alkali distillation chlorolignin gives a product which gives iodoform with iodine and alkali.

12. The mechanism of chlorination can be explained by assuming that lignin has a mol. wt. of 816.

13. No structural formula for lignin so far proposed can adequately explain the above reactions.

I take this opportunity of gratefully acknowledging my indebtedness to my Professors Dr. J. K. Chowdhury and Dr. J. C. Ghosh for the kind interest they have taken in this work.

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The Alkaloids of *Holarrhena Antidysenterica*. Part III. Studies in the Action of BrCN on Conessine and its *N*-Demethylation to *iso*Conessimine and Conimine.

By Salimuzzaman Siddiqui and Rafat Hussain Siddiqui.

The controversy which has till recently existed about the uniformity of conessine since its isolation by Haines as far back as 1858, is a measure of the confusion which has arisen through the sudden multiplication of the minor alkaloids of *Holarrhena antidysenterica* within the last few years, particularly when one takes into account the similarity between the analytical data and the physical properties of some of the 11 new bases isolated by the different authors (*cf.* Table, Siddiqui, *J. Indian Chem. Soc.*, 1934, **11**, 286). The only possibility of effectively clearing up this confusion appeared to lie in the establishment of the exact nature of relationship between the different bases, especially in reference to conessine. The *N*-methylation of conessimine, *iso*conessimine and conimine to conessine (Siddiqui, *loc. cit.*) was the first and a definite step in this direction. The present paper mainly deals with a reversal of this process, namely the *N*-demethylation of conessine to *iso*conessimine and conimine by the saponification of the corresponding cyanamides, obtained through the action of BrCN on conessine and cyano*iso*conessimine respectively, after von Braun's general method of degrading tertiary to secondary amines, which was also used by him in obtaining the *N*-demethylated bases in the morphine series (*Ber.*, 1914, **47**, 3312)

A detailed study of the action of BrCN on conessine leads to the following conclusions in the light of von Braun's exhaustive investigations in the action of BrCN on tertiary amines on the one hand (*Ber.*, 1902, **35**, 1279, and preceeding papers) and Späth's formula for conessine on the other (*Ber.*, 1930, **63**, 126).

$$C_{21}H_{31}\begin{matrix} /\!\!/ NMe \\ \diagdown NMe_2 \end{matrix}$$

(1) That one of the two tertiary amino groups in the conessine molecule corresponds in its intensity of reaction to the type of the pure aliphatic amines, in so far as the monocyanamide is obtained in a quantitative yield immediately on bringing together the components in ethereal solution in the cold.

$$3C_{24}H_{40}N_2 + 2BrCN = 2C_{23}H_{37}N_2{\cdot}CN + C_{24}H_{40}N_2(CH_3Br)_2$$

(2) The second tertiary amino group, very probably with the ring N, containing only one methyl, is comparatively very resistant against the action of BrCN, requiring about a week at room temperature for the completion of the reaction:

$$2\,C_{23}H_{37}N_2{\cdot}CN + BrCN = C_{22}H_{34}N_2{:}(CN)_2 + C_{23}H_{37}N_2{\cdot}CN{\cdot}CH_3Br$$

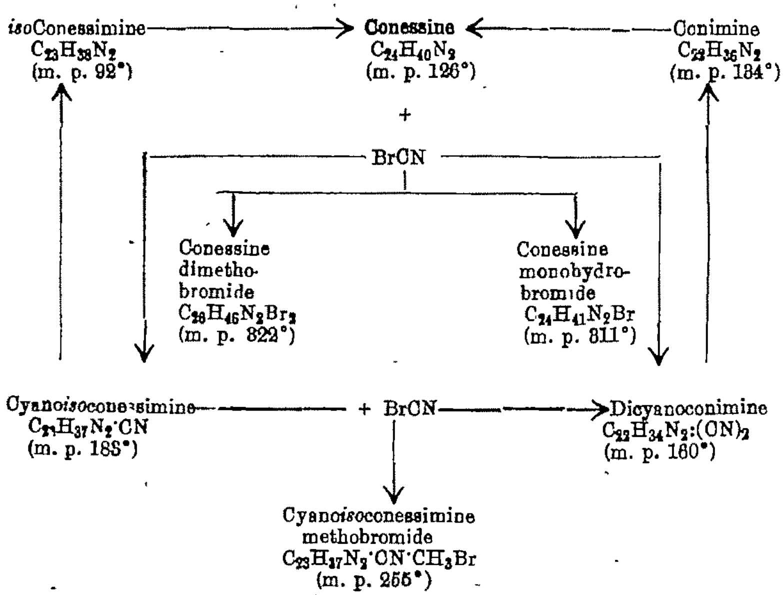
On the basis of these conclusions we feel justified in provisionally according the formula (I) for cyano*iso*conessimine, (II) for *iso*conessimine, (III) for conessimine, (IV) for dicyanoconimine and (V) for conimine.

$$C_{21}H_{31}\begin{matrix}:NMe\\ \cdot N\ Me\ (CN)\end{matrix} \quad (I) \qquad C_{21}H_{31}\begin{matrix}:N(Me)\\ \cdot NHMe\end{matrix} \quad (II) \qquad C_{21}H_{31}\begin{matrix}:NH\\ \cdot NMe_2\end{matrix} \quad (III)$$

$$C_{21}H_{31}\begin{matrix}:N\ CN\\ \cdot N(CNMe)\end{matrix} \quad (IV) \qquad C_{21}H_{31}\begin{matrix}:NH\\ \cdot NHMe\end{matrix} \quad (V)$$

The fact that the monocyanamide (I) and the dicyanamide (IV) yielded on saponification bases whose mixed melting points, optical activities, analytical data proved them to be identical with *iso*conessimine and conimine respectively, finally dissolves every doubt about their purity. A full characterisation of *iso*conessimine and conimine, through their acetyl, benzoyl and nitroso derivatives which was postponed in Part II, has, therefore, been included in this paper. That no trace of cyanoconessimine was found to have been formed under the most varied experimental conditions for the BrCN reaction, agrees with the observation of von Braun that the action of BrCN is quantitatively in one direction and does not give rise to a mixture of cyanamides in case of bases containing only carbon and hydrogen in their molecule (*Ber.*, 1907, **40**, 3933).

The exact relationship of the different products isolated in the course of the present investigations is shown in the chart below. (The formation of HBr salts through the action of BrCN on tertiary amines has also been observed and accounted for by von Braun in a number of cases, *Ber.*, 1900, 33, 2728).



Apart from the decisive bearing of the present investigations on the general progress of work in the *Holarrhena* alkaloids, they afford a totally new orientation to studies in the molecule of conessine and various aspects of the problem are already being investigated ...

EXPERIMENTAL.

... 1 mol.) of BrCN (freshly
... 50 c.c. ether were

was shaken with acetic acid and the acid fraction made alkaline with caustic soda without first boiling off the ether, when a white silky crystalline mass separated out, which after a single crystallisation from a mixture of ether and petroleum ether, yielded 11 g. of pure cyano*iso*conessimine (yield theoretical).

The acetic acid-insoluble ethereal fraction gave just a trace of a treacle on removal of the solvent but no dicyanoconimine could be isolated from it. On refluxing 1 mol. of conessine (1·5 g.) with 2 mols. of BrCN (0·8 g.) in ethereal solution only 0·1 g. of dicyanoconimine could be isolated from the acid-insoluble and 0·4 g. cyano*iso*conessimine from the acid-soluble ethereal fraction. Substitution of chloroform for ether as a solvent for this reaction lowered the yields of both cyano*iso*conessimine and dicyanoconimine, their mother liquors yielding undefinable reddish treacly products. When 1 mol. (21 g.) of conessine was refluxed with only 1 mol. (6·3 g.) of BrCN in chloroform solution for an hour and the reaction mixture worked up in the general sense of the method given above, 3·5 g. of cyano*iso*conessimine, 0·8 g. of dicyanoconimine, 8 g. of conessine dimethoxybromide and (on fractional crystallisation of the residue from the mother liquors of the quarternary ammonium compound from ethyl acetate) 2·6 g. of conessine monohydrobromide were obtained.

Action of BrCN *on cyano*iso*conessimine.*—Attempts to obtain a satisfactory yield of dicyanoconimine through the direct action of BrCN on conessine having failed, the action of BrCN on cyano*iso*conessimine was tried in different solvents under varying conditions. The only method that gave quantitative results was the following.

2 G. of cyano*iso*conessimine were dissolved in 20 c.c. of dry ethyl acetate, a solution of 0·6 g. BrCN in 10 c.c. ethyl acetate added to it and the mixture kept well corked at room temperature ... few hours clusters and stars of large spike-form... crystals of cyano*iso*conessimine methobrom... to separate out. (Found: N, 8·80

Characterisation of the Products of BrCN *Reaction.*

*Cyano*isoco*nessimine.*—It is easily soluble in alcohol, chloroform and benzene, less so in ethyl acetate and acetone, difficultly soluble in ether and insoluble in petroleum ether. It crystallises from absolute alcohol, in which it is not very easily soluble, in elongated plates with angular edges, and from ether and ethyl acetate in plates (m.p. 182-83°). Having only one basic N, it is monoacidic and rectangular forms a single series of salts. [Found: N, 11·09; CH_3, 8·09. $C_{23}H_{37}N_2{\cdot}CN$ requires N, 11·18; (for $2N{\cdot}CH_3$) CH_3, 8·17 per cent].

The hydrochloride was obtained by adding ether to a solution of the base in alcoholic HCl as an oil which crystallised from a mixture of alcohol, ether and petroleum ether in clusters of tapering needles melting at 289-90° (decomp.). It is easily soluble in alcohol, fairly so in hot water, acetone and insoluble in ether. (Found: Cl, 9·09. $C_{23}H_{37}N_2{\cdot}CN$, HCl requires Cl, 8·79 per cent).

The chloroplatinate was obtained by adding a solution of platinic chloride to the aqueous solution of the hydrochloride as a golden yellow powder, insoluble in water but fairly soluble in hot methyl alcohol from which it crystallised out on slow cooling in tufts of slender needles, m. p. 210-11° (decomp.). [Found: Pt, 17·53. $(C_{23}H_{37}N_2{\cdot}CN{\cdot}HCl)_2{\cdot}PtCl_4$ requires Pt, 17·07 per cent].

The picrate was obtained by adding ethereal solution of picric acid to a solution of the base in methyl alcohol as an oily treacle, turning into a bright yellow microcrystalline powder (m.p. 139-40°) on rubbing with hot water. It is easily soluble in methyl alcohol, ethyl acetate and acetone, difficultly soluble in absolute alcohol or water and insoluble in ether.

Dicyanoconimine.—Its solubility in different organic solvents is very similar in character to that of cyano*iso*conessimine. It crystallises from ether, ethyl acetate and acetone, also from concentrated solutions of absolute alcohol in elongated plates with angular edges and melts at 159-60°. Being neutral in character, it does not form any salts and is insoluble in acids and alkalis. [Found: N, 13·47; CH_3, 4·11. $C_{22}H_{34}N_2(CN)_2$ requires N, 14·66; (for $1N{\cdot}CH_3$) CH_3, 3·93 per cent].

Conessine dimethobromide.—It crystallises from a mixture of alcohol and ethyl acetate in prismatic rods and plates which melt at 321-22° (decomp.). It is easily soluble in alcohol, chloroform and

water. From its aqueous solution it separates on addition of caustic soda in wooly flakes and can be shaken out with chloroform [Found: N, 5·08; Br, 29·6; CH_3, 14·8. $C_{24}H_{40}N_2(CH_3Br)_2$ requires N, 5·13; Br, 29·3; (for 5*N*-CH_3) CH_3, 18·7 per cent].

Conessinc monohydrobromide.—It is easily soluble in alcohol and water and difficultly soluble in acetone and ethyl acetate, from which it crystallises in prismatic-rods melting at 310-11° (decomp.). [Found: CH_3, 11·0; Br, 19·0. $C_{24}H_{40}N_2$, HBr requires (for 3 CH_3) CH_3, 10·3; Br, 18·3 per cent].

*Saponification of cyano*iso*conessimine.*—5 G. of cyano*iso*conessimine in 50 c.c. of 20% absolute alcoholic potash were refluxed on the water-bath for 48 hours, in the course of which a crystalline mass slowly separated out, which was identified as potassium carbonate. The slightly reddish residue left on removal of the major portion of alcohol was extracted with ether and the ethereal solution washed with water and then shaken with acetic acid. The nearly colourless, acidic solution was made alkaline with caustic soda and shaken with ether. On removal of the solvent from the well dried ethereal solution, a colourless treacle was obtained, which crystallised from ethyl acetate in clusters and stars of needles melting at 92°, yield 4 g. On admixture with *iso*conessimine from the bark, it did not show any depression in its melting point. With conessimine it began to soften at 70° and completely melted at 80°. In agreement with *iso*conessimine from the plant it showed a rotation, $[\alpha]_D^{28°} = +30°$ in 1% absolute alcohol solution.

Derivatives of iso*Conessimine.*

*Benzoyl*iso*conessimine.*—0·3 G. of *iso*conessimine was finely powdered with 0·12 g. of benzoic anhydride and the mixture which melted at 55° was slowly heated in a sulphuric acid bath up to 140°. After cooling the hard slightly reddish molten mass was dissolved in acetic acid, the acidic solution made alkaline with caustic soda and shaken with ether. The treacle left on removal of the solvent from the dried ethereal solution was taken up in petroleum ether, treated with moist carbon dioxide to remove traces of unreacted base and the colourless solution dried over potassium carbonate. The treacle left on distilling off the solvent yielded the benzoyl base on crystallisation from acetone in aggregates of elongated plates, m.p. 159-60°, yield 0·2 g. It is soluble in alcohol and ethyl acetate,

slightly less so in acetone, ether and petroleum ether and is a mono-acidic base in character. (Found: C, 79·5; H, 9·85; N, 6·16. $C_{23}H_{37}N_2 \cdot CO \cdot C_6H_5$ requires C, 80·7; H, 9·42; N, 6·28 per cent).

The hydrochloride was obtained as a crystalline powder, easily soluble in alcohol, water and acetone by adding ethereal hydrochloric acid to an ethereal solution of the base, m.p. 325-26° (decomp.).

The chloroplatinate was obtained by adding 10% platinic chloride solution to an aqueous solution of the hydrochloride as an amber coloured powder, difficultly soluble in alcohol and insoluble in water, m.p. 264-65° (decomp.). [Found: Pt, 18·5. $(C_{23}H_{37}N_2 \cdot CO \cdot C_6H_5, HCl)1\frac{1}{2}\ PtCl_4$ requires Pt, 18·4 per cent].

Acetylisoconessimine.—0·25 G. of *iso*conessimine hydrochloride and 0·5 g. of sodium acetate were dissolved in 2 c.c. water and 0·6 g. of acetic anhydride added to the solution, which was then heated on the water-bath for an hour. The reaction mixture was cooled, diluted with water, made alkaline with caustic soda and shaken with ether. The residue from the ethereal solution was taken up in petroleum ether and treated with moist carbon dioxide to remove any unreacted base, when a little brownish scum separated out. The colourless solution was dried over potassium carbonate and the filtrate concentrated, when the pure acetyl base separated out in aggregates of rectangular plates, yield 0·15 g. melting at 127-28° and easily soluble in alcohol, ethyl acetate, acetone and ether, less so in petroleum ether. (Found: C, 78·82; H, 10·66; N, 7·65. $C_{23}H_{37}N_2 \cdot CO \cdot CH_3$ requires C, 78·1; H, 10·4; N, 7·29 per cent).

The hydrochloride was obtained by adding ethereal hydrochlric acid to an ethereal solution of the base as a white microcrystalline powder which is soluble in alcohol and water and melts at 325-26° (decomp.). Acetyl*iso*conessimine hydrochloride as prepared by adding an ethereal solution of acetyl chloride to an ether solution of *iso*conessimine also melted at 325-26°. (Found: Cl, 9·58. $C_{23}H_{37}N_2 \cdot CO \cdot CH_3, HCl$ requires Cl, 8·64 per cent).

The chloroplatinate was obtained by adding 5% platinic chloride solution to the aqueous solution of the hydrochloride as an amber coloured powder, which shrinks at 246° and melts at 265-66° (decomp.). [Found: Pt, 21·02. $(C_{23}H_{37}N_2 \cdot CO \cdot CH_3, HCl)\ 1\frac{1}{2}\ PtCl_4$ requires Pt, 20·2 per cent].

Thus both benzoyl and acetyl*iso*conessimines agree with acetyl conessemine (Part II, *loc. cit.*) in forming chloroplatinates answering to the type (B, HCl) $1\frac{1}{2}PtCl_4$.

Nitrosoisoconessimine.—A concentrated solution of sodium nitrite was added in drops to a cooled solution of the base (0·2 g.) in acetic acid with constant stirring. The white granular precipitate was washed with a little water and dissolved in excess of acetic acid, the base liberated with caustic soda and extracted with petroleum ether. On drying the solution over potassium carbonate and concentrating the filtrate, nitroso*iso*conessimine crystallised out in the cold in spike-formed amber coloured needles, m. p. 163-64°, yield 0·12 g. It is soluble in ether, alcohol and acetone, difficultly soluble in petroleum ether and behaves as a monoacidic base. (Found: C, 74·71; H, 10·08; N, 10·94. $C_{23}H_{37}N_2 \cdot NO$ requires C, 74·4; H, 9·97; N, 11·3 per cent).

The hydrochloride, prepared from the components in ethereal solution, formed a crystalline powder which is soluble in alcohol and water and melts at 248-51° (decomp.). (Found: Cl, 9·33. $C_{23}H_{37}N_2 \cdot NO$, HCl requires Cl, 8·92 per cent).

The picrate was obtained from the components in ethereal solution as a bright yellow powder, which crystallised from methyl alcohol in clusters of lemon-yellow tapering needles, which are difficultly soluble in cold, fairly in hot water or alcohol and melt at 190-94°.

Saponification of Dicyanoconimine: Conimine.

2·2 G. of dicyanoconimine was refluxed with 20% absolute alcoholic caustic potash solution (40 c.c.) for 12 hours, when crystals of potassium carbonate slowly separated out. The reddish residue left on removal of the alcohol was extracted with ether. The ethereal solution was washed with water and shaken with dilute acetic acid, from which the base was liberated with caustic soda and extracted with ether. The pale treacly residue, left on removing the solvent from the dried ethereal solution, crystallised from ethyl acetate in clusters and stars of spike-formed needles, yield 1·3 g. It melted at 134° and showed no depression in its m. p. on admixture with conimine from the plant. The melting points of the hydrochloride and the picrate of the base also concurred with those of conimine. It showed a rotation $[\alpha]_D^{30°} = -30°$ in 1% solution in absolute alcohol.

Derivatives of Conimine.

Dibenzoylconimine.—To a solution of 0·5 g. of conimine in 8 c.c. pyridine was added 0·5 g. of benzoyl chloride in a little ether with

cooling and the reaction mixture was left at room temperature for 8 hours. On dilution with water clusters of spindle shaped needles were obtained, which on recrystallisation from chloroform and acetone melted at 250°. It is easily soluble in chloroform, alcohol and ethyl acetate, difficulty soluble in acetone and insoluble in ether and petroleum ether. [Found: C, 79·41; H, 8·23; N, 5·31. $C_{22}H_{34}N_2$ $(CO \cdot C_6H_5)_2$ requires C, 80·60; H, 8·21; N, 5·22 per cent].

Diacetylconimine.—An intimate mixture of conimine (0·5 g), anhydrous sodium acetate (0·5 g) and acetic anhydride (1 c.c.) was heated on the water-bath for 3 hours. The reaction mixture on dilution with water gave a treacly residue which was extracted with ethyl acetate and dried over sodium sulphate. On removal of the solvent the colourless residue was dried in vacuo over P_2O_5 when a semicrystalline snow white powder (0·4 g.) was obtained, which was soluble in hot petroleum ether, ethyl acetate, alcohol and chloroform, insoluble in ether and melted at 139-40°. [Found: C, 75·67; H, 9·79; N, 6·75. $C_{22}H_{34}N_2(CO \cdot CH_3)_2$ requires C, 75·72; H, 9·71; N, 6·79 per cent].

Dinitrosoconimine.—A concentrated solution of sodium nitrite was added in drops to 1 g. of conimine in 5 c.c. of 10% acetic acid with good cooling and stirring. On keeping the mixture for 1 hour at room temperature a viscous oil separated which turned into a powder on rubbing and washing with acetic acid and then with water. On concentrating a solution of the powder in acetone, nitrosoconimine was obtained in aggregates of rectangular plates (0·9 g.) melting at 206-07°. It also crystallises from alcohol or benzene. It is easily soluble in acetone, ethyl acetate, benzene, chloroform and alcohol and insoluble in ether, petroleum ether and water. [Found: N, 14·17. $C_{22}H_{34}N_2$ $(NO)_2$ requires N, 14·5 per cent].

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Studies in the Coagulation of Colloids. Part X. Viscosity Variations during Mutual Coagulations of Positive Ferric Oxide Sol and Colloid Arsenious Sulphide, Manganese Dioxide, and Antimony Sulphide.

By Shridhar Sarvottam Joshi and K. P. N. Pannikkar.

A review of the literature on the subject showed that but little quantitative information is available on the kinetics of the mutual coagulation of oppositely charged colloids, and especially about the corresponding changes of viscosity. It has been shown in previous work (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329 ; Joshi and Menon, *ibid.*, 1933, **10**, 599 ; Joshi and Nanjappa, *ibid.*, 1934, **11**, 133) that during the *slow* coagulations of a number of sols due to different electrolytes, the viscosity increases discontinuously, and also that in a number of well ascertained cases (Joshi and Nanjappa, *loc. cit.* ; Joshi and Iyengar, *ibid.*, 1934, **11**, 555), the above property actually decreased below the initial value. This suggested that the viscosity change is not necessarily a measure of coagulation at any rate in the *slow* region. Since this appeared to be contrary to the current views on the subject, it appeared desirable to examine the validity of the above deduction from the standpoint of a new type of evidence ; to this end, for reasons mentioned already, measurements of viscosity changes during *mutual* coagulations were undertaken.

Experimental.

Colloid ferric oxide was prepared by hydrolysing an aqueons solution of about 5 g. of ferric chloride in a litre. It was dialysed against repeated changes of hot water, till the dialysate was free from chlorine. The colloid content was estimated as in Part VII (Joshi and Nanjappa, *loc. cit.*). The arsenious and antimony sulphide

sols were prepared and estimated for their strengths as described in Parts I and II (*J. Indian Chem. Soc.*, 1931, **8**, 11, 337). The manganese dioxide sol was prepared as recommended by Cuy (*J. Phys. Chem.*, 1921, **25**, 415). The colloid contents per litre of these sols were 1·5 g. Fe_2O_3, 3 g. As_2S_3, 2·1 g. MnO_2 and 1·9 g. Sb_2S_3. The viscosity was measured by Scarpa's method with modifications described previously (Joshi and Vishwanath, *loc. cit.*). The temperature of the thermostat was kept constant at 35° ± 0·1. The suction applied was 27 cm. of water, and kept constant within 0·3 mm. This was such that the time of rise and fall for the constant volume of the liquid was approximately the same. Other details of manipulation and precautions have been described in Parts VI-VIII. On repeated measurements with a standard liquid like water at the above temperature the apparatus used was capable of giving an accuracy of 0·15%. Changes in viscosity *at least* four times as great only are reported.

40 C. c. of the mixture were placed in the Scarpa tube in all the experiments. It contained 20 c. c. of the ferric oxide sol in experiments referred to in Tables I, III and IV. Different volumes of any of the oppositely charged colloid, *viz.*, As_2S_3, MnO_2 and Sb_2S_3, were then diluted with such amounts of water that the volume of the diluted sol was always 20 c. c. (*cf.* 2nd column in Tables I-IV). The two sols were allowed to attain the temperature of the thermostat before mixing. Experiments in Table II refer to coagulations when the amount of colloid ferric oxide was varied and that of arsenious sulphide kept constant. Results for η, the viscosity, have been expressed relative to that of water taken as unity, and have been shown graphically in Figs. 1-8. Results quoted in Tables I-IV have been obtained from the corresponding viscosity-time curves. The following abbreviations have been used: η_i = initial viscosity ; η_m = first minimum viscosity ; η_d is percentage diminution, *i. e.*, $(\eta_m - \eta_i)/\eta_i \times 100$; $T\eta_m$ is time in minutes corresponding to η_m. Remarks in the last column relate to observations of coagulation or otherwise, as judged by the production of the characteristic turbidity some times accompanied by minute particles of the coagulum. Curve Nos. shown in circles in Figs. 1-8 and in 1st column in Tables I-IV refer to mixtures where coagulation was observed. Viscosity measurements were continued, until the coagulum tended to make the system appreciably heterogeneous, and leave a deposit on the walls of the viscometer.

TABLE I.

Colloid content: (*i*) 1·5 g. Fe_2O_3 per litre; (*ii*) 3·0 g. As_2S_3 per litre.

Expt. No.	Composition of the mixture in c. c. $Fe_2O_3 + As_2S_3 +$ Water.	η_i.	η_m.	η_d.	$T\eta_m$	Remarks.
1	20 + 20 + Nil	1·04	1·03	1·25	89	No sensible flocculation in several hr. after mixing.
2	20 + 16 + 4	1·07	1·06	—	13	No sensible flocculation in 2 hrs.
3	20 + 15 + 5	1·11	1·03	6·5	25	Do
4	20 + 12 + 8	1·09	—	—	—	
5	20 + 10 + 10	1·06	—	—	—	Coagulation after 54 mins.
6	20 + 5 + 15	1·05	1·06	—	16	
7	20 + 2 + 18	1·09	—	—	—	
8	20 + 1 + 19	1·09	—	—	—	Immediate coagulation after mixing.
9	20 + 0·5 + 19·5	1·03	—	—	—	Do

TABLE II (*cf.* Fig. 1).

Colloid content: (*i*) 3 g. As_2S_3 per litre; (*ii*) 1·5 g. Fe_2O_3 per litre.

Curve No.	Composition of the mixture in c. c. $As_2S_3 + Fe_2O_3 +$ Water.	η_i.	η_s.	η_d.	$T\eta_m$.	Remarks.
1	20 + 18 + 2	1·06	1·03	2·7	55	No sensible coagulation.
2	20 + 15 + 5	1·07	1·03	2·0	21	
3	20 + 10 + 10	1·05	1·03	2·2	33	
4	20 + 5 + 15	1·08	1·04	4·5	22	
5	20 + 2 + 18	1·17	1·15	1·9	16	
6	20 + 1 + 19	1·05	1·04	1·1	14	
7	20 + 0·5 + 19·5	1·04	1·02	1·8	80	

TABLE III (*cf.* Fig. 2).

Collid content: (*i*) 1·5 g. Fe_2O_3 per litre; (*ii*) 2·1 g. MnO_2 per litre.

Curve No.	Composition of the mixture in c. c. $Fe_2O_3 + MnO_2 +$ Water.	η_i.	η_m.	$\eta_a^\cdot$.	$T\eta_m$.	Remarks.
1	20 + 20 + Nil	1·05	1·04	1·0	12	
2	20 + 15 + 5	1·04	1·03	0·4	22	No sensible flocculation in 2 hours.
3	20 + 12 + 8	1·03	1·03	0·4	14	Immediate coagulation.
4	20 + 10 + 10	1·05	1·03	2·2	33	Immediate coagulation.
5	20 + 1 + 19	1·03	1·01	2·1	14	
6	20 + 0·5 + 19·5	1·03	1·01	2·0	39	

TABLE IV (*cf.* Fig. 3).

Colloid content: (*i*) 1·5 g. Fe_2O_3 per litre; (*ii*) 1·9 g. Sb_2S_3 per litre.

Curve No.	Composition of the mixture in c. c. $Fe_2O_3 + Sb_2S_3 +$ Water.	η_i.	η_m.	η_a.	$T\eta_m$.	
1	20 + 10 + 10	1·08	1·05	3·0	18	Coagulation sensible after 5 mins.
2	20 + 6 + 14	1·05	1·04	1·5	14	
3	20 + 5 + 15	1·18	1·10	0·7	21	Coagulation sensible after 50 mins.
4	20 + 4 + 16	1·04	1·02	1·2	13	
5	20 + 2 + 18	1·03	1·03	1·0	29	No sensible coagulation.

DISCUSSION.

Data in Tables I-IV show that the occurrence of mutual coagulation is not produced for all the proportions in which the two oppositely charged colloids are mixed. This agrees with the results of Biltz (*cf.* Freundlich, "Colloid and Capillary Chemistry," 1926, p. 478) obtained with mixtures of the As_2S_3 and Fe_2O_3 sols that (*a*) coagulation was generally favoured when their colloid contents were approximately equal, and that (*b*) the change was slow to appear and appreciably restricted in bulk when there was a preponderating excess of one of the two constituents. Since in the present experiments the strength

of the As_2S_3 sol is twice as great as that of the Fe_2O_3 sol, it is to be anticipated that coagulation would not be sensible, unless the concentration of the former sol is reduced to half by dilution with water before mixing with the other colloid. The absence of coagulation in experiments recorded in Table II and in Nos 1-4 in Table I, and its appearance from No. 5 onwards is in agreement with the above deduction. It is also seen that as suggested by (*b*), results in Tables III and IV show that coagulation occurs only for an intermediate range of proportions of the two colloids. In this connection, it is somewhat surprising to note from results in Table I that coagulation was both distinct and quick to appear even though the amount of the As_2S_3 sol was reduced to as low as 0·5 c. c. (and diluted with 19·5 c. c. of water), while that of the Fe_2O_3 sol was 20 c.c.

It is seen from the foregoing results that a decrease of viscosity in the range 0·7 to 6·5% of the initial viscosity occurs in 22 out of 27 coagulations studied, within 16 to 39 minutes (in one, 55) after mixing the colloids. The η-time curves (not shown in fig.) corresponding to experiments No. 4, 5, 7 and 8 in Table I showed that viscosity increased rapidly during these coagulations, and that the initial viscosity diminution was insensible, as observed in numerous instances of *rapid* coagulation reported previously (*cf.* Parts VI-IX, *loc. cit.*). It would appear however that although the present results confirm the frequent occurrence of an initial fall of viscosity as observed in the considerable number of *slow* coagulations studied previously (*loc. cit.*), more experimental work is needed to elucidate the nature of the micellar and other changes connected with its occurrence. It might be mentioned that the magnitude of the initial fall of viscosity observed in some of these *mutual* coagulations is considerably larger than that observed in *electrolytic* coagulation studied previously. It was also observed (*cf.* Joshi and Iyengar, *loc. cit.*) that unlike a definite stage in coagulation whose duration is highly influenced by changes in the nature and strength of the coagulator, the time corresponding to the occurrence of the initial fall of viscosity varies but irregularly over not a wide range of time. It is interesting in this connection to observe that (*cf.* Table II) appreciable values of η_m are observed although there is no sensible coagulation. This suggests that the process (or processes) accessory to this initial diminution of viscosity is nearly as widely occurrent as coagulation itself, and in all probability independent of the latter (*vide infra*).

Fig. 1.

$As_2S_3 + Fe_2O_3$ sols.

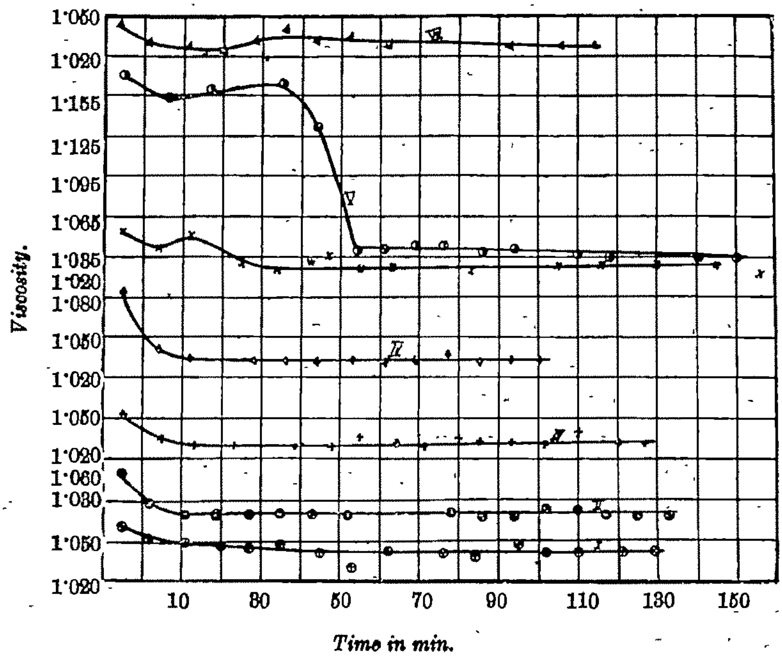
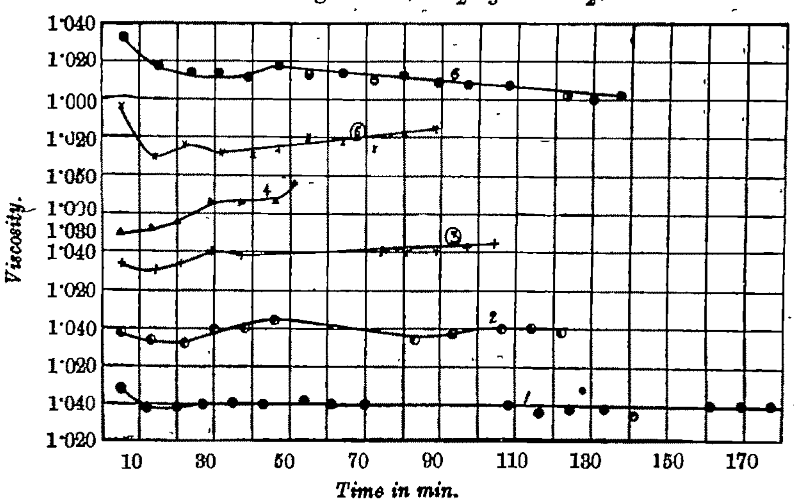


Fig. 2.

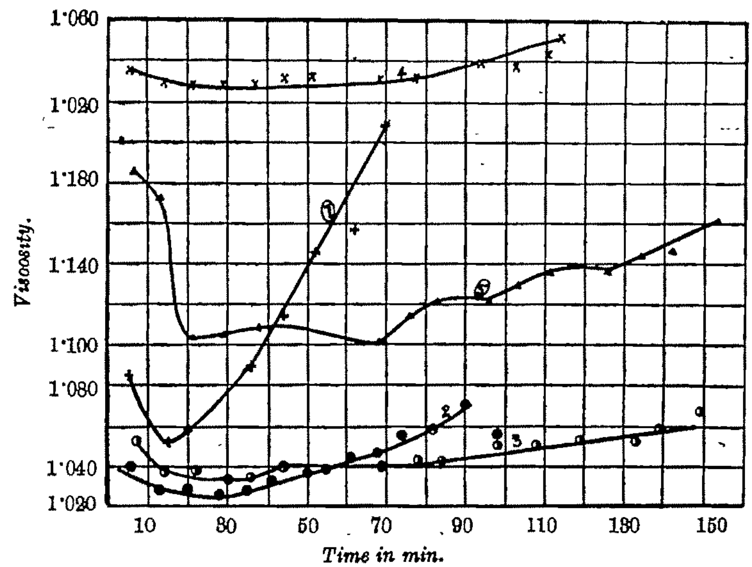
Mutual coagulation, $Fe_2O_3 + MnO_2$.



Coagulation distinct in curves 3&5.

Fig. 3.

Mutual coagulation, $Fe_2O_3 + Sb_2S_3$.



Coagulation distinct in curves 1&5.

An examination of the viscosity-time curves in Figs. 1-3 shows that the last remark is also applicable to viscosity changes η_d produced as a result of mixing the oppositely charged colloids. Moreover, in agreement with results in previous publications (*loc. cit.*) the time variation of the viscosity of the mixed colloids is, in general, *discontinuous*, except when the coagulation is *rapid*. It is also notable that though comparatively more uniform, the viscosity variations are quite appreciable in magnitude even in mixtures where no coagulation could be observed. In experiments No. 7 and 8 corresponding to two successive mixtures in Table I coagulation was observed only in the latter. The corresponding viscosity-time curves (not shown in figure) showed however an essentially similar type, *viz.*, an initial rapid rise to a well marked maximum and a subsequent decrease. Additional evidence in this connection is provided by the series of mixtures to which curves in Fig. 1 refer; these show the occurrence of sensible viscosity variations not accompanied by coagulation (*cf.* other curves in Figs. 2 and 3). *Similar* results, to be published shortly, have been obtained in numerous coagulations

due especially to the use of *non-electrolytes* as coagulators. It might be recalled that quite a considerable part of the current evidence in the literature for the production of coagulation depends upon visual observation of the turbidity and allied changes such as flocculation. Thus defined, coagulation corresponds to but an intermediate region in the series of changes limited on one extreme by the precipitation of the suspended material, and on the other, by the just incipient, perhaps pre-coalescence changes in the micelle initiated on the introduction of but traces of the coagulant. It is to be anticipated therefore that a typical colloid-sensitive property like viscosity should be influenced by changes not sufficiently gross to be noticed under coagulation observed visually by noting turbidity changes. Incidentally, this shows the necessity of following the progress of a given coagulation by more than one of the properties employed generally in these measurements. Such work has been already in progress for some considerable time in these laboratories, and the results will be reported in due course.

SUMMARY.

1. Mixtures of positively charged colloid ferric oxide with varying proportions of negative arsenious sulphide, manganese dioxide and antimony sulphide sols have been studied for mutual coagulation and consequential viscosity changes. The former was *usually* noticeable for certain intermediate proportions of the two colloids.

2. Sensible viscosity changes were produced even when there was no preceptible coagulation. These changes, in agreement with previous results, showed an *initial fall* of viscosity up to 6·5 per cent. of the initial value, and well marked *discontinuities* on the viscosity-time curves. Both these features tended to disappear in *rapid* coagulations.

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Thermionic Emission and Catalytic Activity. Part II. Thoria-Ceria Surfaces. A Contribution to the Theory of Welsbach Gas Mantle.

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Various theories have been put forward to account for the increase in the light emissivity of the gas mantle containing 99·1% thoria and 0·9% ceria. Lewis (*Chem. News*, 1905, **91**, 62) gives a complete summary of the work done so far on the subject. Westphal, suggested that the emissivity is due to the combination of an acidic oxide like thoria with that of a basic one like ceria. But Bunte (*cf.* Lewis, *loc. cit.*) put forward the idea that the mantle surface is catalytically active and the chemical reaction of the burning gases on the surface heats up the refractory material to such high temperatures that the glow occurs. In order to produce light emissivity of such magnitude as in the gas mantle, Rubens (*Ann. physik*, 1906, *iv*, **20**, 593) has shown that a black body temperature of at least 1600° is required. However, Le Chatelier and Boudouard (*Compt. rend.*, 1898, **126**, 1861) found that thoria-ceria mixtures exhibited unequal emissivity for different regions in the visible part of the spectrum and that these mixtures conformed more to a coloured body radiator. Nernst and Bose (*Physikal. Z.*, 1900, **1**, 289) also found that these mixtures gave rise to selective radiation when heated in a Bunsen flame. Bunte later abandoned his catalysis theory and preferred the radiation theory on the basis of the results of his co-workers, Schmidt and others who showed that the light emissivity of the mantle was the same as that of the mixture even though heated to the same temperature in a muffle furnace. The experimental method of these authors has been objected to by Lewis (*loc. cit.*).

On the other hand White and Travers (*J. Soc. Chem. Ind.*, 1902, **21**, 1012) maintains that the temperature of heating has no correlation with light emissivity. A thoria surface heated up to 1510° gave only 1·2 C. P. per cu. ft. of gas, while a mantle surface at 1404° gave 15·7 C. P. per cu. ft. They consider that a solid solution of ceria in thoria occurs, which exhibits a maximum efficiency in converting

heat into light. That a solid solution of ceria in thoria occurs is confirmed well by the experiments of Meyer and Anschutz (*Ber.*, 1907, **40**, 2639). M. Chas. Ferry (*Ann. chim. phys.*, 1902, *vii*, **27**, 433) thinks that ceria is finely divided and dispersed as a solid solution in thoria and helps to increase the catalytic activity of thoria by condensing the gases on the surface and that the chemical reaction gives rise to the high temperature and luminosity.

Recently Swan (*J. Chem. Soc.*, 1924, **125**, 780) has shown that the maximum catalytic efficiency of ceria-thoria mixtures towards electrolytic gas mixtures is also found to occur with a surface containing 0·8% of ceria. He concluded that ceria acts as an oxygen-carrying promoter to the catalyst material thoria (*cf.* Wyrouboff and V. B. Lewis, Taylor, "Catalysis in Theory and Practice," 1926, p. 199) or increases the electron emission of thoria, which causes greater ionisation of the reacting gases. He leaves the question open between these two possibilities. Even if the first alternative is taken in preference to the latter, there is no reason why a mixture containing only 1% of ceria should show maximum catalytic activity and luminosity.

In Part I of this series (*Indian J. Phys.*, 1931, **5**, 685) the author has drawn attention to the complete analogy that exists between thermionic emission and catalysis and has further shown that the interaction between carbon dioxide and hydrogen on the surfaces of platinum and thoriated tungsten was perceptible at the same temperature at which thermionic emission was also evident. It appears interesting to connect the two sets of observations by attributing thermionic emission as the primary cause of chemical reaction at the surfaces of incandescent bodies.

The example of the Welsbach gas mantle forms an interesting study in this connection. It is the object of this paper to study in a comparative way the emission of electricity from a platinum wire coated with mixtures of ceria and thoria of different amounts and see if the maximum thermionic emission from these surfaces occurs also at the same proportion of thoria and ceria (99 : 1), which is known to give maximum light emissivity and catalytic efficiency.

EXPERIMENTAL.

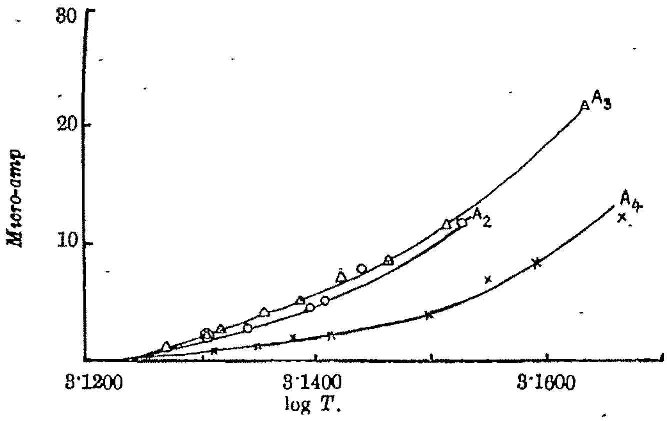
The apparatus and the experimental methods are exactly the same as in the previous part (*loc. cit.*), except that the spiral MacLeod

gauge was replaced by the more common form. A complete discussion of the limitations of the experimental methods are to be found there. The heating current in this case is supplied by a 10 volt battery through a rheostat. In measuring thermionic currents a micro-ammeter was used for the platinum wire and a sensitive galvanometer of the D'Arsonval type was used for the wires coated with thoria-ceria mixtures. In order to minimise the table leak, all the pieces of the measuring instruments were set on ebonite sheets. The table was heavily waxed with paraffin. The key switch in the galvanometer circuit was put on by means of a long ebonite rod.

Coating of the wires.—Weighed quantities of the nitrates of thorium and cerium, which would give the required proportion of thoria-ceria on ignition, were dissolved in the minimum quantity of water and mixed. The platinum wire was dipped in the syrupy solution and was heated outside by a small current to dull red glow, when the nitrates decomposed leaving a thin coating of the mixed oxides. This process was repeated carefully twice or thrice till a uniform and an adherent coating was obtained.

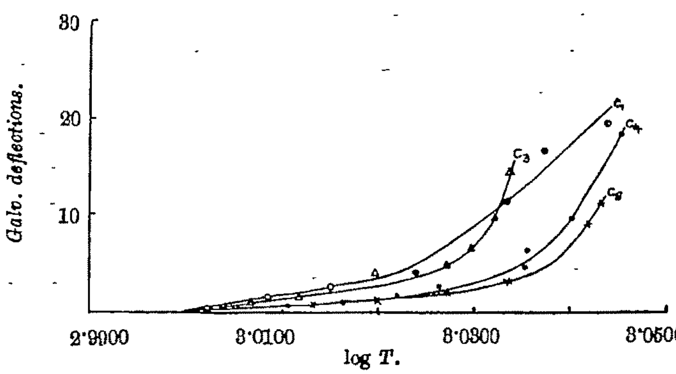
Temperature measurement.—The temperature of the hot wire was calculated from a knowledge of its resistance. The resistance of the wire at the melting point of ice and steam was measured with a Robertson bridge with compensating leads joined to 1 cm. of platinum wire in the circuit. This allows sufficiently for the cooling effect at the leads while the wire is heated. The resistances of the wire at the higher temperatures were calculated by noting the heating current in the circuit and the voltage across the ends of the wire. A sensitive ammeter and a voltmeter were employed. The temperature coefficient of resistance of the platinum wire was $88{\cdot}4 \times 10^{-4}$. For the coated wires the temperature coefficient was assumed to be the same as that of platinum, since thoria and ceria are poor conductors of heat. The resistances of the wire calculated from these data could be taken with confidence and an error of even 0·01 ohm in the neighbourhood of 1000° makes only a difference of less than 5° in the calculated temperature. Hence the temperature measurements are quite reliable.

FIG. 1.



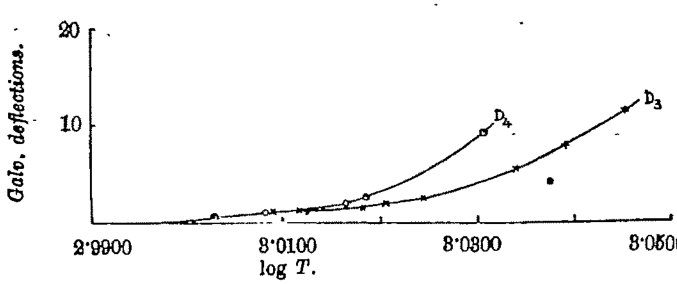
Pt. wire. log $T = 3{\cdot}1285$. $T = 1329°$.

FIG. 2.



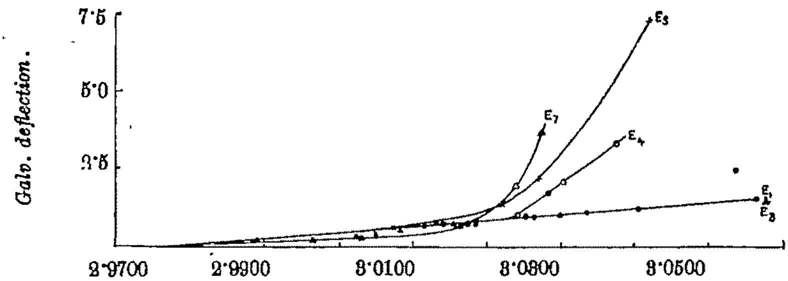
Thoria : ceria : : 98·83 : 1·17. log $T = 2{\cdot}9996$ $T = 999{\cdot}5°$.

FIG. 3.



Thoria : ceria : : 99·12 : 0·88. log $T = 2{\cdot}9990$. $T = 909{\cdot}6°$.

FIG. 4.



Thoria : ceria : : 98·97 : 1·03. log $T = 2·9770$. $T = 948°$.

Figs. 1-4 present the summary of the results on thermionic emission from platinum and platinum coated with thoria-ceria mixtures of varying composition. As in the previous work the temperatures at which thermionic emission is just perceptible or commences was found for each of these surfaces. The logarithms of the temperatures of the glowing wires were plotted against the galvanometer deflection. Duplicates agree well as seen from the graphs. These graphs are straight lines at low temperatures and when produced cut the X-axis sharply at the same point. But at higher temperatures they suddenly bend and go up. This is due to large currents being set up owing to ionisation due to collision with the gases evolved in the tube during the course of the experiment. Quantitative measurement of electron emission at any one temperature for each of these surfaces was not made but a comparision of the temperatures at which the emission was perceptible for these surfaces was made. That surface which at any temperature would exhibit maximum emissivity over the others would give rise to incipient emission at a far lower temperature than that of the others. Table I gives the temperatures (to the nearest degree) obtained from the graphs at which thermionic emission is just perceptible over various thoria-ceria surfaces.

TABLE I.

Surface.		Temperature at which thermionic emission is just perceptible.
Platinum	... ...	1329°
Thoria-ceria	98·83 : 1·17	1000°
Do	98·97 : 1·03	948°
Do	99·12 : 0·88	1000°

It is seen from the results that the temperature at which thermionic emission is perceptible is minimum with a thoria-ceria surface containing 98·97% of thoria and 1·03% ceria. Consequently this surface should give rise to maximum electron emission in comparision with others. This result when considered with those of the light emissivity of the gas mantle and that of the catalytic activity of thoria-ceria (*loc. cit.*) provides an interesting basis for the explanation of activation of gases at catalytic surfaces and in particular the light emissivity of incandescent mantles. On the basis of the results obtained here and in the previous part (*loc. cit.*), it could be definitely stated that the activation of gases on the surfaces of catalysts depends on the capacity of the surface to emit electrons. The light emissivity of the gas mantle is a consequence of the oxidation of kerosene hydrocarbons on the surface of the mantle which is also dependent on the electron emission. A further discussion on the theoretical bearing of the catalytic activation of gases on the electron emission of the catalyst will form the subject of another communication.

SUMMARY.

1. A review of the various theories put forward to explain the brilliance of the Welsbach gas mantle is made.

2. Comparative measurements of thermionic emission from the surfaces of platinum, and thoria-ceria mixture of varying percentages, are made.

3. A mixture of thoria-ceria containing 1% of ceria is found to give rise to incipient electron emission at a lower temperature than those containing more or less amounts of ceria than 1%; this is identified to give the maximum electron emission than the other mixtures at the same temperature.

4. Catalytic activation of gases, of which the example of the Welsbach gas mantle is a particular case, is definitely attributed to electron emission from that catalyst surface.

My thanks are due to Principal Rao Bahadur G. Nagaratnam, B.A., B.E., M.I.E., for his kind interest and to Mr. S. Rengachari, B.A., for his kind assistance.

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Attempts to Synthesise Uric Acid from Nine-membered Cycloids.

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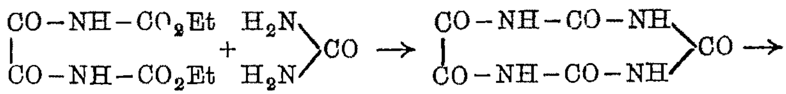
The syntheses of uric acid known at present involve reactions which are many and complex, the starting material itself being not easily obtained in some cases. Horbaczewski's synthesis (*Ber.*, 1882, **15**, 2678 ; *Monatsh*, 1885, **6**, 356; 1887, **8**, 206) which at present is of interest merely as being the first, was to heat urea with glycocoll or cyanacetic acid; but Hoffmann (*Annalen*, 1925, **441**, 215) asserts that "not a trace of uric acid is formed by heating urea with glycocoll".

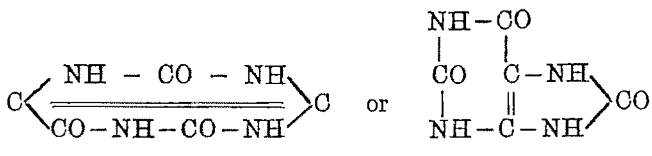
For all the syntheses of uric acid and purine bases, Behrend and Roosen (*Ber.*, 1881, **21**, 999; *Annalen*, 1888, **251**, 235), Baeyer and Schlieper (*Annalen*, 1863, **127**, 3), Fischer (*Ber.*, 1895, **28**, 2473; 1897, **30**, 559), Traube (*Ber.*, 1900, **33**, 1871, 3085), John (*J. Amer. Chem. Soc.*, 1909, **41**, 58; 1911, **45**, 79) have first prepared a 4:5-disubstituted pyrimidine derivative and then built up the iminazole ring from the substituent groups in the 4:5-positions. It, therefore, seemed that if uric acid or any of its more closely allied derivatives could be synthesised from a simple nine-membered cycloid, the suggestion that similar syntheses take place within the living organism from the polypeptides, which are known to be among the degradation products of proteins in the body, would gain probability. Apart from this, any simple synthesis of uric acid or its derivatives would possess an intrinsic interest and also might be useful for the preparation of some of the important purine derivatives occurring in plant products, such as caffeine, theobromine, theophylline, etc. The methods, which have now been tried to achieve this end, differ fundamentally from the earlier syntheses by attempting to bridge a nine-membered cycloid in such a way that the required pyrimidine and iminazole rings come into existence simultaneously, as they exist in the uric acid molecule.

Three distinct methods of attacking the problem were planned. The first was to condense oxalyldiurethane with urea to produce

carbo-oxalyldiurea (I) which on reduction might yield uric acid (II)

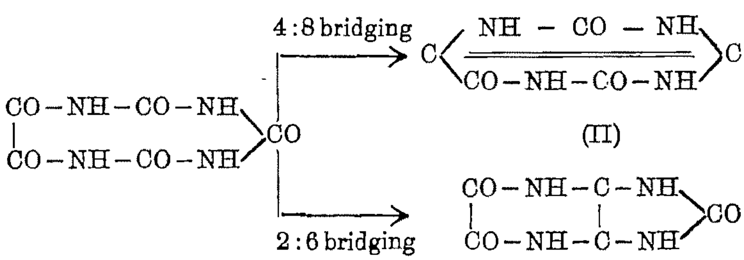


(I)



(II)

The possibility of bridge formation on reduction of carbo-oxalyldiurea might now be considered. The removal of the oxygen atoms from positions 2:4, 2:9, 4:6 and 6:8 would lead to the formation of three-membered rings, and from 6:9 a four membered ring which are not likely to be stable and hence their formation improbable. While there is undoubtedly the possibility of the 2:6-linkage, by far the most stable system would result from the linking of the 4:8 carbon atoms (or what amounts to the same thing, between 4:9) giving rise simultaneously to a five and a six-membered ring. It was expected that reduction of carbo-oxalyldiurea would yield a mixture of products (II) and (III).



(III)

The hydrolysis of oxalyldiurethane to the corresponding diacid was first attempted in the expectation that the latter would be more reactive than the ester, and be condensible with urea in presence of phosphorus oxychloride, analogous to Grimaux's synthesis of malonylurea. Alkalis and acids of various strengths under varying conditions were tried as hydrolysing agents but in every case there was complete disruption of the molecule into carbon dioxide,

ammonia and oxalic acid. Finally carbethoxy-oxamic acid, $CO_2H{\cdot}CO{\cdot}NH{\cdot}CO_2Et,\ 3H_2O$ (IV) was isolated by using hydrochloric acid (1:6) and it is surprising that a compound of such simple structure is now obtained for the first time.

The hydrolysis of oxalyldiurethane to oxalodicarbamic acid having failed, it became necessary to attempt the direct condensation of urea with oxalyldiurethane.

From an equimolecular proportion of oxalyldiurethane and urea heated at 120-25° for eight hours it has been possible to isolate the expected carbo-oxalyldiurea (I), carbethoxyoxamide $CO_2Et{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$ (V), dicarbamyloxalyldiurethane (VI), an alkali-soluble white sandy powder (VII, m p. above 340°), and allophanic ester. Carbethoxyoxamide is evidently formed from oxalyldiurethane by hydrolysis and decarboxylation during the process of isolation of the products.

The compound believed to be dicarbamyloxalyldiurethane (m.p. 230°) would be formed according to the following scheme:

$$
\begin{array}{l}
\qquad CO_2Et \\
\quad\ \diagup \\
CO-NH \\
| \\
CO-NH \\
\quad\ \diagdown \\
\qquad CO_2Et
\end{array}
\begin{array}{c}
\\ \\ NH_2-CO-NH_2 \\ + \\ NH_2-CO-NH_2 \\ \\ \\
\end{array}
\longrightarrow
\begin{array}{l}
\\ \\ CO-N(CO_2Et)-CO-NH_2 \\ | \\ CO-N(CO_2Et)-CO-NH_2 \\ \\ \qquad\qquad (VI)
\end{array}
$$

It does not respond to biuret test. On treatment with alkali it yields ammonia, alcohol and sodium oxalate.

The infusible compound (VII) responds to the biuret test and yields ammonia with boiling caustic alkali. Without any further experimental proof it is not possible at this stage to attribute to it any definite structure.

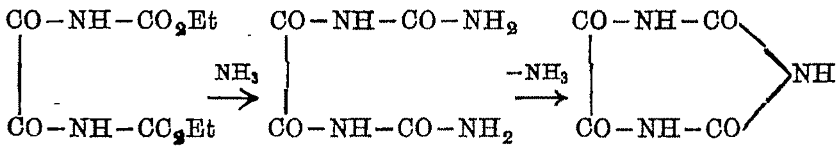
From one molecule of oxalyldiurethane and more than two molecules of urea at a fusion temperature (135-40°) there has been obtained oxalyldibiuret (VIII), besides other products not examined.

$$
\begin{array}{l}
CO-NH-CO_2Et \\ | \\ CO-NH-CO_2Et
\end{array}
+
\begin{array}{l}
NH_2-CO-NH_2 \\ \\ NH_2-CO-NH_2
\end{array}
\longrightarrow
$$

$$
\begin{array}{l}
CO-NH-CO-NH-CO-NH_2 \\ | \\ CO-NH-CO-NH-CO-NH_2
\end{array}
+ \ 2EtOH
$$

(VIII)

In an attempt to prepare oxalyl diurea from oxalyldiurethane and ammonia we have obtained oxalylbiuret (VIII*a*) besides the expected diurea, which evidently loses a molecule of ammonia:

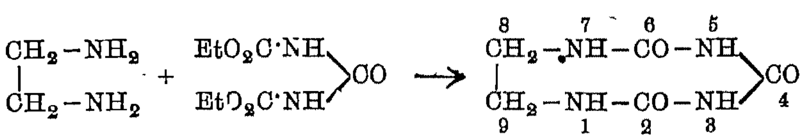


(VIII*a*)

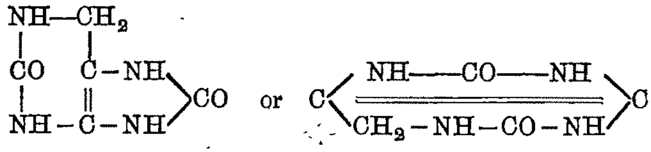
A similar attempt to prepare the amide of hydantoic acid, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$, from urethaneacetic ester by the action of the ammonia resulted in the formation of a monoamide (m.p. 105°), isomeric with hydantoic ester, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$ (m.p. 135°), and having the probable constitution, $CO_2Et \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$.

Direct bridge formation by reduction of the carbonyl groups in position 4:8 or 4:9 of carbo-oxalyldiurea has been tried without success by (*a*) exposing a mixture of the substance and alcohol in a sealed tube to sunlight (*cf. Ber.*, 1900, **33**, 2912), (*b*) sodium and moist ether (*cf.* Perkin and Kipping, *J. Chem. Soc.*, 1891, **59**, 218) and (*c*) zinc dust and alcoholic potash (*cf.* Beschke, *Annalen*, 1909, **369**, 184), these being mild reduction processes for effecting internal pinacone condensation; more drastic methods of reduction have not been tried, being evidently unsuitable. A promising line of approach will be electrolytic reduction, which has been used successfully for a variety of substances related to the purines (*cf.* Tafel, *Ber.*, 1901, **34**, 258, 1165, 3286; *Ber.*, 1900, **33**, 3383; Knorr and Klotz, *Ber.*, 1886, **19**, 3300; Wollers, *Annalen*, 1902, **324**, 279).

Meanwhile, scarcity of the requisite materials turned our attention to the synthesis of carboethylenediurea (IX) which on dehydration should give desoxyuric acid (X) thus:



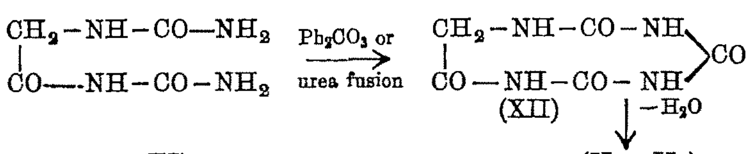
(IX)



(X)

It is presumed that the methylene hydrogen in position 8 or 9 would condense with the carbonyl oxygen in position 4 in preference to those in position 2 or 6, the product in either case being desoxy-uric acid. Removal of water from the oxygen of the carbonyl groups in position 2 or 6 and hydrogen from 8 or 9 is less likely, as the latter would result in the formation of the unstable three-and four-membered systems. By using boiling concentrated hydrochloric acid, a product supposed to be desoxyuric acid (X) and showing the characteristic properties of uric acid was obtained. This compound is not known, though Tafel (*Ber.*, 1901, 34, 250) suggested its formation as a transient intermediate product during the electrolytic reduction of uric acid into purine.

The third method planned for the synthesis of uric acid was analogous to the synthesis of desoxyuric acid by dehydration of carboglycollyldiurea. The problem, in the first instance, is, therefore, to synthesise glycollyldiurea (XI), which by the action of urea or phenyl carbonate could be converted to carboglycollyldiurea (XII).—

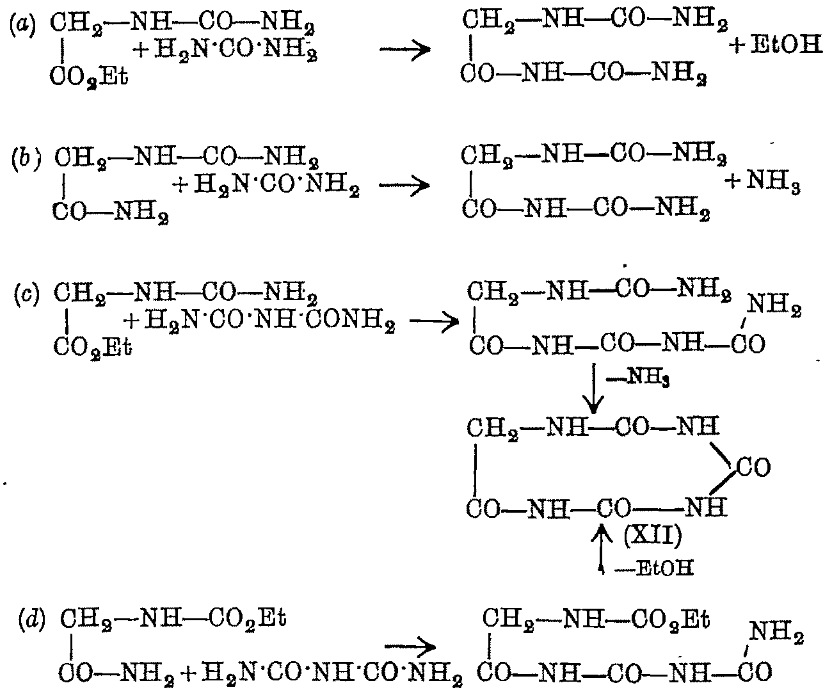


(XI) (II or II*a*)

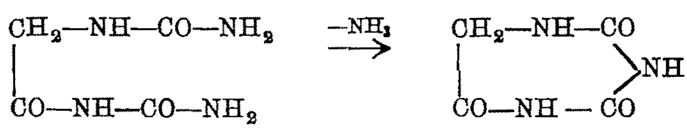
Eppiger (*Beitr. Z. Chem. Physiol. u. Pathol.*, 1905, 6, 287) claims to have obtained glycollyldiurea (m.p. 158°) by the action of sulphuric acid and potassium cyanate upon the amide of hydantoic acid. The original paper being not available, the preparation was tried according to the method available in the abstract (*Chem. Zentrl*, 1905, 1, 947) more than a dozen times under different conditions and with varying quantities of material, but only cyanuric acid could be isolated.

The action of urea upon hydantoic ester or amide and of biuret upon urethaneacetamide or hydantoic ester was next tried in the

hope of obtaining glycollyldiurea from the first two reactions and carboglycollyldiurea from the third and the fourth.



The first reaction has yielded hydantoin and cyanuric acid together with a very small quantity of a crystalline yellow substance, m. p. 236°, agreeing in composition with the expected glycollyldiurea (XI) $C_4H_8O_3N_4$ and a fourth substance glycollylbiuret (XIII) which appears to have been formed from glycollyldiurea by the loss of a molecule of ammonia.



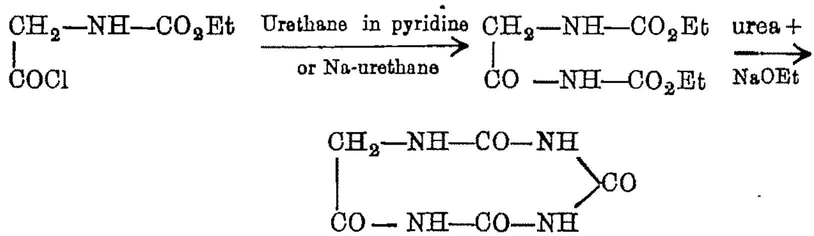
(XIII)

The conversion of hydantoic ester and amide into hydantoin by the action of heat, acid and alkali is well known.* Hydantoin itself has now been found to react with urea to give a small yield of glycollyldiurea in analogy with the formation of oxalyldiurea from parabanic acid and urea (Biltz and Topp, *Ber.*, 1913, **46**, 1404;

Grimaux, *Bull. Soc. chim.*, 1879, *ii*, **32**, 100; Bornwaler, *Chem. Zentrl.*, 1912, **II**, 910, 1739).

The biuret reactions have not yielded the desired product; a yellow crystalline compound (m. p. above 340°, N, 35·71%) has, however, been isolated besides cyanuric acid from the hydantoic ester reaction.

These fusion reactions having proved not very useful for the preparation of carboglycollyldiurea in the workable yield, attempts are being made to produce these substances from carbethoxyglycine chloride of Fischer and Otto (*Ber.*, 1903, **36**, 2107), as follows:



(XII)

The action of urea with carbamidoacetic acid in presence of condensing agents like acetic anhydride, $POCl_3$, fuming sulphuric acid, etc., is being investigated (*cf. Ber.*, 1900, **33**, 1380, 3034; 1908, **41**, 530; *Annalen*, 1904, **335**, 364) and with hydantoic ester in presence of sodium ethylate (*cf.* D. R. P. 165224, 193446, 158553; *Annalen*, 1905, **340**, 336) in the hope of producing satisfactory yield of glycollyldiurea. The result of these investigations will form the subject of a subsequent communication.

EXPERIMENTAL.

Improved method of preparing oxalyldiurethane.—Oxalyldiurethane could not be obtained in a satisfactory yield by the previous methods (Hantzsch, *Ber.*, 1894, **27**, 1250; Priestley, *J. Chem. Soc.*, 1909, **95**, 453; Diels, *Ber.*, 1903, **36**, 739). To sodium wire (7·5 g.) suspended in dry benzene (200 c.c.) was added dry powdered urethane (25 g.). The reaction commenced immediately and became quite vigorous after about three quarters of an hour when there was much frothing. The flask was cooled in ice-water and occasionally shaken. After 24 hours ethyl oxalate (43 g.) was added to the sodium urethane for 15 minutes with frequent shaking, the temperature being not allowed to rise above 0° and after about an hour

the flask was allowed to attain the room temperature. The pasty mass, formed on the addition of 4*N*-sulphuric acid (200 c. c.), hardened to a light colourless solid on being cooled with ice. This was filtered at the pump, thoroughly washed with water to remove the last trace of sodium sulphate and then crystallised from about 500 c. c.of 80% alcohol. On standing overnight in an ice-chamber, colourless glistening plates of oxalyldiurethane were deposited, m. p. 172°, yield 28 g.

Hydrolysis of oxalyldiurethane.—Oxalyldiurethane (2 g.) was heated under reflux with potassium hydroxide solution (25 c. c.) of strengths *N*, 2*N* and 4*N*, on a water-bath for periods varying from ½-3 hours. The clear solution after cooling was neutralised in each case with dilute hydrochloric acid and evaporated to dryness on the water bath. The absolute alcoholic extract of the colourless residue gave on concentration colourless crystals of oxalic acid, m.p. 98°, mixed m. p. remaining undepressed.

Carbethoxyoxamic acid (IV).—Oxaldiurethane (2 g.) was heated under reflux with 60 c.c. of dilute hydrochloric acid (1:6) for 1½ hours on a water bath with occasional shaking and the solution evaporated to dryness. The colourless solid residue could after various attempts be freed from oxalic acid by repeatedly (8-9 times) washing with anhydrous methyl alcohol. A solution of the residual solid in the minimum quantity of hot water gave on standing for 3-4 hours at 0° colourless crystals, m. p. 133-34°, yield 1 g. The substance is very soluble in water at ordinary temperature and in alcohol, but sparingly soluble in ice-cold water and in methyl alcohol. It is soluble in alkalis and in sodium carbonate. (Found: C, 27·62; H, 6·58; N, 6·28. $C_5H_7O_5N, 3H_2O$ requires C, 27·90; H, 6·11; N, 6·51 per cent).

Oxalyldiurethane and urea.—An intimate mixture of dry oxalyldiurethane (80 g.) and urea (12 g.) was heated at 120-25° for 8 hours with occasional stirring when ammonia was evolved. The molten, pale yellow mass frothed gently and drops of liquid condensed on the sides of the flask. On cooling, the contents became a pale yellow, hard solid which after being well powdered was digested repeatedly with 80 % alcohol. The alcoholic extract deposited on cooling a microcrystalline solid (A), the mother liquor (B) being almost colourless.

Allophanic ester.—(A) separated from 10 % acetic acid in colourless crystals, m. p. 188-89°, yield 6 g., identified by mixed melting

point and analysis as allophanic ester (Found: N, 21·23; Calc. N, 21·2 per cent).

Carbethoxyoxamide (V).—The mother liquor from allophanic ester on being concentrated to about one quarter its bulk gave a crystalline deposit which after repeated crystallisation from water yielded colourless glistening plates, m.p. 155-56°, yield about 2 g. The substance is fairly soluble in alcohol, sparingly so in water and insoluble in ether. (Found: N, 17·64. $C_5H_8O_4N_2$ requires N, 17·50 per cent).

Carbo-oxalyldiurea (I).—The acetic acid filtrate after the isolation of allophanic ester deposited on concentration lemon-yellow crystals, which after being washed with water was repeatedly crystallised from a small quantity of dilute acetic acid, m. p. above 300°, yield about 5 g. (Found: N, 28·06, 27·92. $C_5H_4O_5N_4$ requires N, 28·01 per cent). It responds to the biuret reaction and on hydrolysis with alkali is readily decomposed into ammonia, carbon dioxide and oxalic acid.

The main portion of the reaction product was a yellow, noncrystalline solid left after alcohol extraction and was purified by precipitating it several times with concentrated hydrochloric acid from its solution in 2*N*-sodium hydroxide. The precipitation does not appear to be quantitative and takes place slowly on standing. The substance does not melt even at 330°. The purity of the substance was established by the identical analytical values obtained from different samples. (Found: N, 35·47, 35·69. $C_5H_{10}O_5N_6$ requires N, 35·89 per cent).

Dicarbamyloxalyldiurethane (VI).—The alcoholic filtrate (B) when evaporated on a water-bath gave a solid which on being crystallised from water gave as the first crop a small quantity of carbethoxyoxamide (m. p. 155-56°); the subsequent crops on being crystallised together from water gave a white crystalline compound, m.p. 230°. (Found: C, 37·41; H, 4·78; N, 17·31. $C_{10}H_{14}O_8N_4$ requires C, 37·73; H, 4·40; N, 17·81 per cent).

Oxalyldibiuret (VIII).—An intimate mixture of oxalylurethane (8 g., 1 mol.) and dry urea (5 g., more than 2 mols.) was heated at 135-40° for 3½ hours. The powdered melt was extracted with boiling water and the filtrate gave on cooling pale yellow crystals, which were boiled repeatedly with alcohol, finally with water and dried at 110°, m.p. 185-86°, yield about 3 g. (Found: N, 32·68. $C_6H_8O_6N_6$ requires N, 32·31 per cent). It gives the biuret test

and is decomposed by boiling alkali into ammonia, carbon dioxide and oxalic acid.

Oxaldiurethane and ammonia: Formation of oxalyldiurea and oxalylbiuret (VIII *a*).—The white precipitate separating out from a mixture of oxalyldiurethane (6 g.) and liquor ammonia (50 c.c.) on standing for 48 hours, was crystallised from a large quantity of water, m.p. above 350°, yield 2 g. (Found: N, 32·06. $C_4H_6O_4N_4$ requires N, 32·18 per cent). It is insoluble in ammonia and hence cannot be cyanuric acid (N, 32·56).

The ammoniacal filtrate gave on evaporation a solid mixed with a pasty liquid from which on alcohol treatment a solid separated. It crystallised from alcohol in shining white needles, m.p. 235°. (Found: N, 27·04. $C_4H_3O_4N_3$ requires N, 26·75 per cent). The alcohol containing the paste gave on concentration and cooling a white crystalline solid, m.p. 140°, yield 0·03 g.

Urethaneacetamide.—The clear solution obtained from a mixture of urethaneacetic ester (10 g.) and liquor ammonia (50 c. c.) after standing overnight gave on evaporation a white solid (m.p. 80-90°) which after repeated crystallisation from alcohol-benzene melted sharply at 105°. (Found: N, 19·27, 19·18. $C_5H_{10}O_3N_2$ requires N, 19·18 per cent).

Hydantoic amide and phenyl carbonate: Formation of glycollylbiuret (XIII).—An intimate mixture of hydantoic amide (5 g.) and phenylcarbonate (18 g.) was heated at 170-180° for 45 minutes, developing the odour of phenol. The unchanged phenyl carbonate and phenol were removed by digesting successively with boiling water and carbon tetrachloride. The residual black tarry mass after being washed with ether was crystallised from alcohol, m.p. 220- 21° (Found: N, 29·67. $C_4H_5O_3N_3$ requires N, 29·37 per cent).

Carboethylenediurea (IX).—To carbodiurethane (50 g., 1 mol.) contained in a 250 c.c. conical flask was added ethylenediamine hydrate (20 g.) and after a few minutes, the carbodiurethane dissolved forming a light orange, viscous solution, which gradually became hot. After about 20 minutes a white solid separated. The contents of the flask were then heated under reflux on a water-bath for about ½ hour, 100 c.c. of water added and then filtered. The residue crystallised from a large quantity of boiling water, m.p. 188-89°, yield 25 g. It was identified as allophanic ester by mixed m.p. and analysis. (Found: N, 21·34. $C_4H_8O_3N_2$ requires N, 21·2 per cent).

The pale yellow filtrate on evaporation on the water-bath left a viscous, light-brown residue which on standing in a vacuum over sulphuric acid for about a fortnight congealed to a jelly-like mass. The latter on being refluxed with methyl alcohol left a white powder which crystallised from a large quantity of water, m.p. 275-76°. The yield was only about 1·5 g. (Found: C, 34·46 ; H, 5·01 ; N, 31·67. $C_5H_8O_3N_4$ requires C, 34·88; H, 4·65; N, 32·55 per cent). The experiment was repeated twice. The methyl alcohol used for refluxing the jelly-like solid deposited on standing some unchanged carbodiurethane.

Dehydration of carboethylenediurea: Formation of desoxyuric acid (?) (X).—Carboethylenediurea (3 g.) was heated with concentrated hydrochloric acid (20 c.c.) under reflux on a water-bath for about 2 hours. The white solid obtained from the solution on evaporation was dissolved in the minimum quantity of 2*N*-potassium hydroxide. The filtered solution after acidification with concentrated hydrochloric acid and on being allowed to stand deposited a colourless solid, yield about 0·6 g. (Found: C, 39·25; H, 4·21 ; N, 36·05. $C_5H_6O_2N_4$ requires C, 38·96 ; H, 3·89 ; N, 36·36 per cent). It was a white sandy powder, soluble in alkalis and in concentrated sulphuric acid. It did not melt even at 340°. On heating the substance over a free flame it did not fuse, but gave urea as one of the decomposition products. On attempting the murexide reaction, a pale yellow to orange-red coloration resulted. This is only to be expected since murexide, formed from uric acid, contains the strong chromophore carbonyl, which in the case of the analogous compounds obtained from desoxyuric acid is replaced by the methylene group. It may be pointed out that the methyluric acids give the murexide reaction so long as the -CO- group referred to above is intact and purone does not give any murexide test at all.

Hydantoic ester and urea: Isolation of glycollyldiurea (XI) *and glycollylbiuret* (XII).—Hydantoic ester was prepared from glycine ester hydrochloride and potassium cyanate according to the method of Haber (*Ber.*, 1900, **33**, 3418). An intimate mixture of hydantoic ester (10 g.) and urea (6 g.) was heated in an oil bath at 130-35° for 6 hours when evolution of ammonia ceased. A hot water extract of the powdered melt gave on cooling a yellowish solid from which hot alcohol extracted a dull yellow substance leaving cyanuric acid undissolved. The yellowish solid on being crystallised twice from the minimum quantity of water was obtained in yellowish plates,

m.p. 236°, yield 0·2 g. (Found: C, 29·6; H, 4·81; N, 35·81. $C_4H_8O_3N_4$ requires C, 30·0; H, 5·00; N, 35·00 per cent).

The filtrate from glycollyldiurea was concentrated to one quarter its bulk from which on cooling there separated a white granular solid, m.p. 215° after crystallisation from alcohol and identified as hydantoin by mixed m.p., yield about 3·5 g.

The original filtrate from hydantoin and the mother liquor obtained during its crystallisation gave a solid on evaporation to dryness which on being repeatedly crystallised from water gave two substances melting respectively at 220-21° and 132°, the latter being urea while the former (yield 0·2 g.) gave the following result on analysis. (Found: N, 29·81. $C_4H_5O_3N_3$ requires N, 29·37 per cent).

Hydantoic amide and urea: Isolation of glycollyldiurea.—The experimental procedure was the same as in the foregoing experiment excepting that hydantoic amide required a longer period (25 hours) of heating. The tarry reaction product was extracted with boiling water, the solution evaporated to dryness and the residue digested with 15 c.c. of alcohol. The filtered alcoholic solution gave on cooling about 0·2 g. of a yellow substance which was purified by crystallising twice from water, m.p. 236°, undepressed on admixture with the product from the foregoing experiment.

Hydantoin and urea: Isolation of glycollyldiurea.—From the melt obtained by heating an intimate mixture of hydantoin (5 g.) and urea (4 g.) only 0·3 g. of the yellow crystalline substance (m.p. 236°) could be obtained.

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The Condensation of Aldehydes with Malonic Acid in Presence of Organic Bases. Part I. In Presence of Pyridine alone.

By P. N. Kurien, K. C. Pandya and V. R. Surange.

The condensation of aldehydes with malonic acid has been extensively studied using such condensing agents as alcoholic ammonia, primary and secondary amines, particularly piperidine (Knoevenagel, *Ber.*, 1898, **31**, 2596 *et* seq.,), pyridine (Verley, *Bull. Soc. chim.*, 1899, **21**, 143; Doebner, *Ber.*, 1900, **33**, 2140; 1901, **34**, 53; 1902, **35**, 1136, 2137; Staudinger, *Bull. Soc. Chim.*, 1927, **41**, 440), pyridine with a trace of piperidine (Haworth, Perkin and Rankin, *J. Chem. Soc.*, 1924, **125**, 1693; Dutt, *J. Indian Chem. Soc.*, 1925, **1**, 297), and other secondary and tertiary bases (Dalal and Dutt, *ibid.*, 1932, **9**, 309).

In this paper various aldehydes, particularly the aromatic hydroxyaldehydes, which gave poor or no yield with pyridine alone, have been condensed with malonic acid and a trace of pyridine.

The condensation of salicylaldehyde with malonic acid could be expected to give three possible products: *o*-coumaric acid (I), coumarin carboxylic acid (II) and coumarin (III).

$$C_6H_4\left\langle\begin{array}{l}OH\\CH{:}CH{\cdot}COOH\end{array}\right.\qquad\qquad C_6H_4\left\langle\begin{array}{l}O\text{——}CO\\CH{=}C{\cdot}COOH\end{array}\right.$$

(I) (II)

$$C_6H_4\left\langle\begin{array}{l}O\text{——}CO\\CH{=}CH\end{array}\right.$$

(III)

It has been found that the condensation proceeds only when a trace of pyridine is present (*vide* Experimental) and gives 51% of coumarin carboxylic acid (II), m.p. 187-89° as was obtained by other methods (Perkin, *J. Chem Soc.*, 1877, **32**, 389; Stuart, *ibid.*, 1886, **49**, 366 and Knoevenagel, *ibid.*, 2585, 2593) and not *o*-coumaric acid (I) m.p. 200°, as reported by Dutt (*loc. cit.*).

The other aldehydes that could be condensed in the same way are mentioned in the Experimental part.

EXPERIMENTAL.

(K. C. PANDYA AND V. R. SURANGE).

In the first experiments pure dried malonic acid (3 g.) was condensed with molecular proportions of aldehyde and of the carefully purified pyridine (3 c.c.), by heating on a boiling water-bath for about 4 hours. The product on cooling was treated with sodium carbonate solution and steam-distilled, the residue acidified with dilute hydrochloric acid and the precipitated acid purified by crystallisation.

TABLE I.

Aldehyde condensed.	Acid obtained.	Yield.	Duration of heating.
Benzaldehyde	Cinnamic acid	89%	4 hrs.
o-Nitrobenzaldehyde	*o*-Nitrocinnamic acid	96	2
m- ,, ,,	*m*- ,, ,,	93	2
p- ,, ,,	*p*- ,, ,,	90	2
Salicylaldehyde	None	0	18
Vanillin	,,	0	6

(P. N. KURIEN AND K. C. PANDYA).

Condensation of salicylaldehyde with malonic acid: Formation of coumarin carboxylic acid.—After various trial experiments using different quantities of pyridine at varying temperatures and changing the duration of heating, the following condition gave the maximum yield of the condensation product.

Salicylaldehyde (6 g.) and malonic acid (5 g.) were heated together for 4 hours on the water-bath. Pyridine (0·5 c.c.) was then added, the flask cooled, and the whole left at 15° for 6 days. The flask was then again warmed at 60-65° for 4-5 hours. The acid then separated in the usual way, m.p. 187-89°. (Found: C, 62·79; H, 3·31. $C_{10}H_6O_4$ requires C, 63·15; H, 3·16 per cent). The silver salt gave an equivalent weight 190·3, while Dutt's acid (I) requires 164 and $C_{10}H_6O_4$ requires 190. The melting point never rose above 189° and it was depressed to 160-65° by admixture with an

authentic specimen of *o*-coumaric acid (I). On heating it gave the smell of coumarin and not of phenol and its barium salt was insoluble.

Ferulic acid.—Vanillin (3·1 g.), malonic acid (2·1 g.) and pyridine (0·3 c.c.) were mixed and heated on a water-bath for 4 hours. On cooling the solid was powdered, shaken with chloroform or treated with sodium carbonate solution and the clear solution acidified with hydrochloric acid. On recrystallisation from water, it melted at 169°, and with solutions of ferric chloride, silver nitrate, lead acetate and Fehling's solution respectively, gave the characteristic reactions of ferulic acid, yield 4 g. (57%).

p-*Hydroxycinnamic acid* (p-*coumaric acid*).—*p*-Hydroxybenzaldehyde (2·4 g.), malonic acid (2 g.) and pyridine (0·8 c.c.) were heated in the usual way for 5 hours. From the liquid product, *p*-coumaric acid, m. p. 207°, was obtained in 88% yield.

m-*Nitrocinnamic acid.*—*m*-Nitrobenzaldehyde (3 g.), malonic acid (2 g.) and pyridine (0·2-0·3 c.c.) were mixed and heated for 4 hours, within half an hour a solid was formed and the acid melting at 198° came out in 92% yield.

p-*Methylcinnamic acid* was obtained from *p*-tolualdehyde (2·3 g.), malonic acid (2 g.) and pyridine (0·2-0·3 c.c.). It melted at 198°, yield 84%.

Cinnamylidenemalonic acid and cinnamylideneacetic acid.—(*a*) Cinnamic aldehyde (3 g.), malonic acid (2·4 g.) and pyridine (3 c.c.) were heated on a water-bath for 1 hour. The solid was dissolved in sodium carbonate solution, the solution acidified when cinnamylidenemalonic acid, m.p. 208° (decomp.) was obtained, yield 90%.

(*b*) In another experiment the heating was continued for 18 hours and cinnamylideneacetic acid, m.p. 165°, was obtained, yield 50%.

β-Benzylcrotonic acid, prepared from hydrocinnamic aldehyde (2·6 g.), malonic acid (2 g.) and pyridine (0·2-0·3 c.c.) by heating for 4 hours, melted at 104°, yield 29%.

p-*Methoxycinnamic acid.*—Anisaldehyde (3·4 g.), malonic acid (2·6 g.) and pyridine (0·2-0·3 c.c.) were heated for 4 hours. It melted at 172°, yield 78%.

Piperonylacrylic acid.—Piperonal (3 g.), malonic acid (2 g.), pyridine (0·2-0·3 c.c.) were heated for 4 hours. It melted at 240° (decomp.), yield 100%.

Furfurylacrylic acid.—Freshly distilled furfural (2·8 g.), malonic acid (2·6 g.) and pyridine (0·2-0·3 c.c.) were heated on a water-bath, the mass immediately turned brown and began to solidify after 3 hours' heating. Heating was continued for 2 hours more, the product separated and purified by crystallisation from hot water, m. p. 136°, yield 73%.

Trichlorocrotonic acid.—Chloral (2·88 g.), malonic acid (2 g.), pyridine (0·3 c.c) were heated on a water-bath at 85° for 5 hours. On cooling a solid separated, which on purification melted at 119°, yield 28%.

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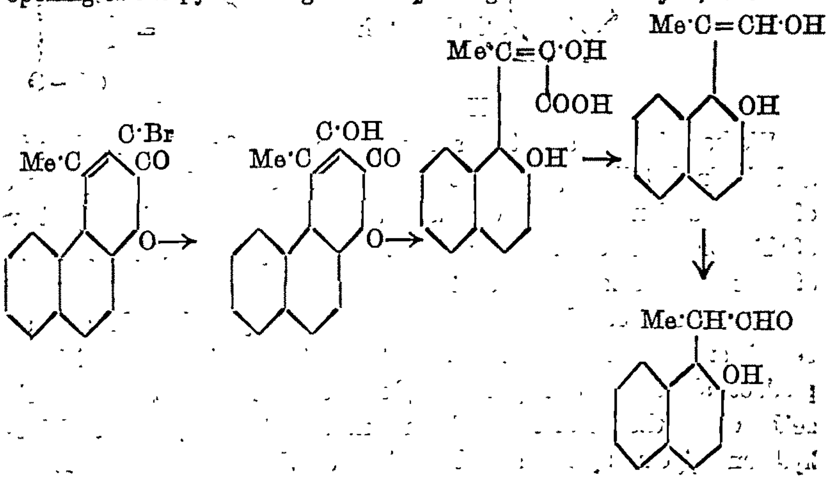
3-Amino- and 3-Hydroxy-β-naphthapyrones.

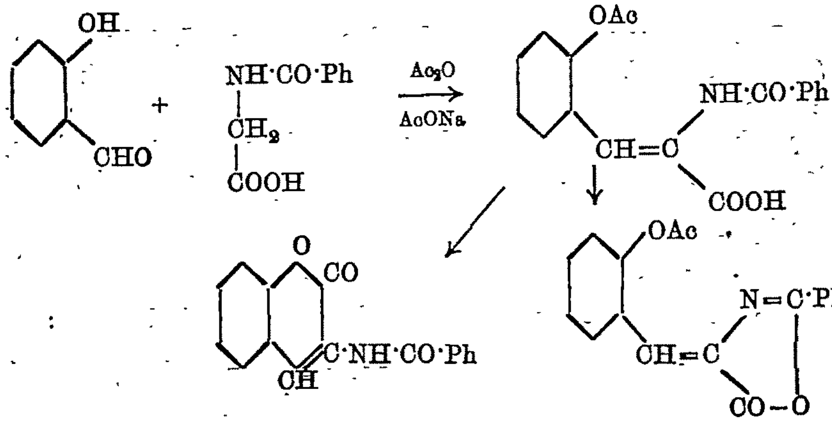
By B. B. Dey and A. K. Lakshminarayanan.

In a previous paper (Dey and Lakshminarayanan, *J. Indian Chem. Soc.*, 1934, 11, 373) it has been shown that the action of alkali on 3-bromo-4-methyl-β-naphthapyrone gives rise to a product of a new type which is believed to be 2-hydroxynaphthyl-1-α-propionic aldehyde, in addition to the known β-naphthafuran carboxylic acid. To explain the formation of this extraordinary compound the suggestion was made that an intermediate 3-hydroxy-β-naphthapyrone was first formed and that the *cis* acid derived from the latter by the opening of the pyrone ring lost CO_2 and gave the aldehyde, thus:



As it seemed that our theory of the mechanism of this reaction could be tested by preparing, if possible, 3-hydroxy-β-naphthapyrones and studying their behaviour with alkalis, we undertook to carry out experiments in this direction and the results of some of these are described in the present communication. It may be stated at the outset that although the synthesis of the unsubstituted 3-hydroxy-β-naphthapyrone has now been accomplished, the treatment with alkali has not produced the desired aldehyde. We cannot definitely say, however, that this failure to obtain the aldehyde from 3-hydroxy-β-naphthapyrone invalidates our original hypothesis, since the methyl group in position 4 in the other naphthapyrone may have exercised an important influence, not taken into consideration in the present case, in determining the course of the change.

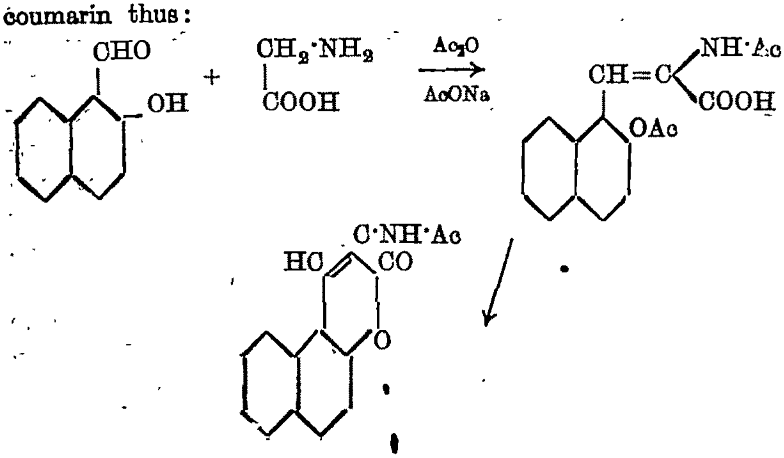
Erlenmeyer and Stadlin (*Annalen*, 1904, 337, 283) have studied the reaction between salicylaldehyde and hippuric acid and shown that a mixture of azlactone (I) and 3-benzoylaminocoumarin (II) are formed thus:



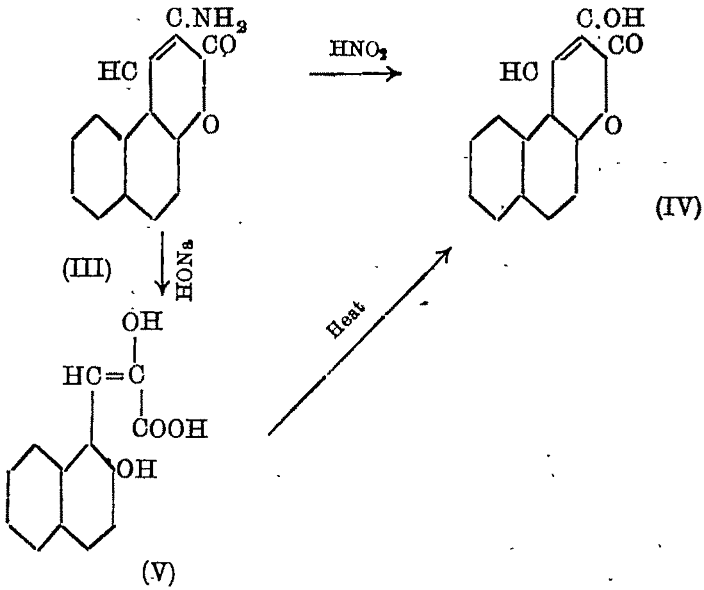
(II) (I)

We have investigated the same reaction with β-naphthol aldehyde and obtained 3-benzoylamino-β-naphthapyrone as the sole product of the reaction unmixed with any azlactone. The debenzoylation of this compound to the free amine was accomplished with a mixture of HBr and glacial acetic acid.

The amine formed a very sparingly soluble hydrochloride and an acetyl and a benzoyl derivative. The latter was identified with the product obtained directly from β-naphtholaldehyde and hippuric acid, while the former has been synthesised from β-naphtholaldehyde and glycine by a method similar to the one used by Linch (*J. Chem. Soc.*, 1912, **101**, 1766) for the preparation of 3-acetylamino-coumarin thus:



The action of nitrous acid on the amine (III) leads to the formation of the desired 3-hydroxy-β-naphthapyrone (IV), the latter being also prepared in good yield through an unstable intermediate *cis* acid (V) by boiling the amine with alkali till the evolution of NH_3 had ceased:



All attempts to convert the *cis* acid into the expected 2-hydroxy-naphthyl acetaldehyde by decarboxylation were, however, fruitless.

We have compared the properties of 3-amino-β-naphthapyrone with those of 3-aminocoumarin prepared by Linch (*loc. cit.*) by the indirect method of subjecting 3-acetylcoumarin oxime (Knoevenagel, *Ber.*, 1889, 31, 732) to the Beckmann change.

Linch assumed that 3-aminocoumarin existed mainly in the tautomerised imino form on the ground that it yielded a nitroso- and a benzylidene derivative. 3-Amino-β-naphthapyrone behaved, however, in the normal manner and we have no grounds for assuming that the compound shows a tendency to tautomerise into the imino-form.

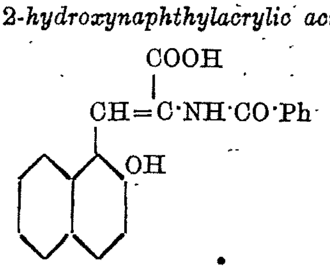
EXPERIMENTAL

3-*Benzoylamino-β-naphthapyrone*.—An intimate mixture of hippuric acid (6 g.), β-naphthol aldehyde (5·9 g.), anhydrous sodium acetate (2·9 g.) and acetic anhydride (12 g.) was heated to

100° for $\frac{3}{4}$ hour and the contents which changed to a hard orange mass on cooling, were broken up, treated with water and filtered. The insoluble matter was washed 6 times with 25 c.c. of ether when it became colourless and melted at 220-26° (5·2 g.). It was practically insoluble in alcohol and dissolved sparingly in glacial acetic acid from which it crystallised in silky needles, m.p. 180°, yield 4 g. The product was insoluble in cold acids or alkalis but on heating with the latter, it dissolved slowly with the evolution of ammonia. A solution of the substance in strong sulphuric acid exhibited a fine blue fluorescence. (Found: C, 76·11; H, 3·94; N, 4·84. $C_{20}H_{13}O_4N$ requires C, 76·19; H, 4·13; N, 4·44 per cent).

The ether washings from the above were dried over $CaCl_2$, the ether evaporated and the orange red oil distilled under reduced pressure. Two fractions were collected: (A), b.p. 132-140°/10 mm. which passed over as a light yellow oil and partly solidified and (B) b.p. 140-160°/10 mm. a colourless oil of a peculiar odour which gradually solidified to a crystalline mass. From (A) by fractional crystallisation from ether and from methanol, colourless needles (m.p. 120°) were finally obtained. These were identified as β-naphthapyrone by a mixed m.p. determination. On working up the mother liquor, a considerable amount of a second substance, m.p. 85°, were obtained which was identified as acetoxy-β-naphthol aldehyde. The crystals separating from fraction (B) crystallised from acetic acid in silky needles, m.p. 230° and were proved to be identical with 3-benzoylamino-β-naphthapyrone, yield 0·8 g. A further quantity (0·3 g.) was obtained by working up the coloured residue in the distilling flask.

trans *a-Benzoylamino-β:2-hydroxynaphthylacrylic acid.*



On acidifying the cold alkaline solution obtained by heating benzoylamino-β-naphthapyrone with 2N-alkali a reddish oil which gradually solidified separated out. It dissolved completely in cold sodium carbonate but was reprecipitated as an oil which solidified

as before and then melted rather indefinitely between 150-90°. It was purified by several crystallisations from dilute methanol as needles, m.p. 206° (decomp.). The coumarin could not be recovered from the product after melting, but the acid was converted into the coumarin both by ultraviolet illumination and by means of concentrated sulphuric acid. The acid is believed, on these grounds, to have the *trans* structure (*cf.* Dey and Lakshminarayanan, *loc. cit.*).

3-*Amino-β-naphthapyrone*.—A solution of the benzoyl compound (2 g.) in glacial acetic acid (60 c.c) was mixed with 20 c.c. of HBr (*d* 1·38) and refluxed on a sand-bath 12 hours. Most of the acetic acid was distilled off, the solution neutralised with 2*N*-ammonia and the separating solid crystallised from alcohol as clusters of needles of a cream colour, m.p. 169°, yield 0·6 g. The same compound was obtained in a much poorer yield by dissolving the benzoyl derivative in ice-cold sulphuric acid and pouring into water after 12 hours and basifying with ammonia. The amine dissolved slowly in dilute mineral acids and gave off ammonia on boiling with alkali. (Found: C, 73·7; H, 4·25; N, 6·78. $C_{13}H_9O_2N$ requires C, 73·9; H, 4·27; N, 6·63 per cent).

The *hydrochloride* was best prepared by passing HCl gas into a solution of the base in dry alcohol as colourless rectangular plates, m.p. 201°, practically insoluble in water. (Found: Cl, 14·0. $C_{13}H_{10}O_2NCl$ requires Cl, 14·3 per cent). The *sulphate* crystallised in sheaves of needles.

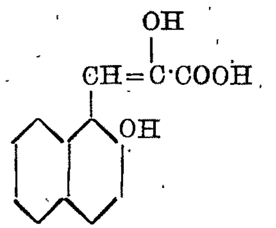
The *acetyl* derivative, prepared by acetylating in presence of a drop of pyridine, crystallises from alcohol in long needles, m.p. 245°. A dilute alcoholic solution shows a beautiful blue fluorescence. (Found: N, 5·67. $C_{15}H_{11}O_3N$ requires N, 5·53 per cent).

The *benzoyl* derivative, prepared in the usual way, crystallises from acetic acid in needles, m.p. 229°, not depressed by admixture with the product synthesised from hippuric acid and β-naphthol aldehyde.

3-*Acetylamino-β-naphthapyrone*.—A mixture of β-naphthol aldehyde (4·4 g.), glycine (2 g.), fused sodium acetate (2·2 g.) and acetic anhydride (10 g.) was heated in an oil-bath at 140° for 5 hours. The dark oil which showed no signs of solidification on leaving in the ice-chest for 24 hours was washed repeatedly with *N*/10-alkali and with 50% alcohol when it changed into a semi-solid mass. This

was dried and rubbed frequently with ether when it became granular, the ether washings being continued till no appreciable colour was removed. The resulting brownish solid was washed with hot alcohol and then crystallised twice from acetic acid (charcoal) as rosettes of cream colour needles, m.p. 245°, yield 0·7 g. It was identified as acetylamino-β-naphthapyrone by a mixed m.p. determination. On heating with HCl (1:2) for a few minutes and basifying with ammonia, the amino-β-naphthapyrone (m.p. 160°) was thrown down in a crystalline condition.

Action of alkali on 3-amino-β-naphthapyrone: cis *α-Hydroxy-β:2-hydroxynaphthylacrylic acid.*



The amine (1 g.) was gently boiled with *N*-alkali (8 c.c.) till NH_3 ceased to evolve. The solution which assumed a golden yellow colour was cooled in ice, neutralised with HCl and the sticky mass, which became granular on standing, purified by dissolving in sodium carbonate and reprecipitation. It crystallised from hot water in plates which sintered at 120° and melted completely at 136° (decomp.). The residue after melting solidified. It was then found to melt at 215-20°. (Found: M.W., 226. $C_{13}H_{10}O_4$ requires M.W., 230).

3-Hydroxy-β-naphthapyrone.—The acid obtained by heating the amino-β-naphthapyrone with alkali was heated at 160° for 10 minutes; the acid melted to a colourless liquid with the evolution of steam and resolidified. It was crystallised from dilute methanol as greenish needles, m.p., 230°, soluble in alkali but insoluble in carbonate. It gave an inky colour with neutral ferric chloride. (Found: C, 73·02; H, 3·80. $C_{13}H_8O_3$ requires C, 73·58; H, 3·77 per cent).

3-Acetoxy-β-naphthapyrone crystallised from alcohol in micaceous plates, m.p. 162°. The crystals themselves exhibited a light blue fluorescence and the solution in alcohol fluoresced powerfully.

(Found: C, 70·8; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·9; H, 4·0 per cent). The *benzoyl* derivative melted at 172°.

Action of nitrous acid on amino-β-naphthapyrone.—To a solution of the amine (0·8 g.) in methanol containing 4*N*-HCl (4 c.c) a solution of sodium nitrite (0·5 g.) was run in drop by drop. The green precipitate was filtered and treated with very dilute alkali when a portion of it dissolved to a deep red solution. The insoluble residue was found to be unchanged amine. The alkaline solution on acidification precipitated brown solid which crystallised from alcohol (charcoal) in needles, m.p. 228°, not lowered by admixture with 3-hydroxynaphthapyrone, m.p. 230°.

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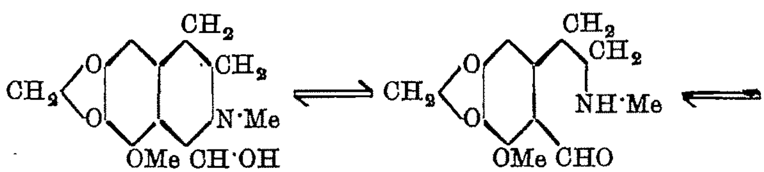
Received June 2, 1934.

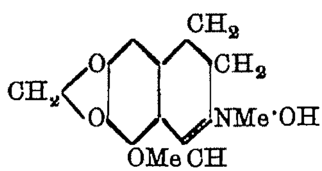
Studies in the Cotarnine Series. Part I. Action of Phenyl *iso*Cyanate and Phenyl *iso*Thiocyanate on Cotarnine.

By B. B. Dey and (Miss) P. Lakshmi Kantam.

The commonly accepted formulæ for cotarnine admit of three tautomeric types, *viz.*, the aldehyde-imine (I), the carbinol (II), and the ammonium hydroxide (III).

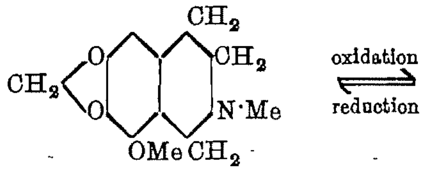


(II) (I)



(III)

Roser (*Annalen*, 1888, **249**, 156; 1889, **254**, 334) assigned to the free base formula (I) and to its hydrochloride the formula of an ammonium chloride derived from (III). That cotarnine was a secondary base as implied in structure (I) was inferred from its reaction with methyl iodide, two methyl groups being taken up in the formation of the quaternary iodide. Evidence of the presence of a free aldehyde group was derived from a study of the action of hydroxylamine both on the free base and on its benzoyl derivative. The easy oxidation to cotarnine of hydrocotarnine which, from its chemical behaviour, cannot have any other structure than (IV), is, however, admittedly difficult of explanation on the basis of Roser's formula, although the reverse change, the reduction of cotarnine to hydrocotarnine, might be readily accounted for.



(I)

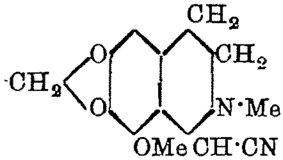
Hydrocotarnine

(IV)

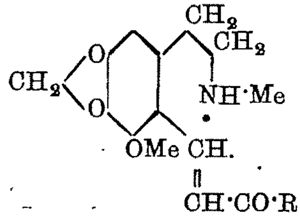
The formula failed also to explain the relationship to cotarnine of certain of its derivatives such as the tarconines and Decker (*J. pr. Chem.*, 1893, **47**, 222) indicated other difficulties in the way of acceptance of Roser's open-chain structure and proposed to substitute for it the carbinol formula (II). This view met with general approval and Hantzsch and Kalb (*Ber.*, 1899, **32**, 3109) who investigated the conductivities of solutions of cotarnine cyanide and cotarnine hydrochloride, suggested that such solutions consisted of a mixture in equilibrium probably of Decker's carbinol form and the ammonium hydroxide form.

The spectroscopic investigations (Dobbie, Lauder and Tinkler, *J. Chem. Soc.*, 1903, **83**, 598) have favoured the conclusion that cotarnine has normally the carbinol formula but changes rapidly in aqueous or alcoholic solution into the ammonium hydroxide, yielding ultimately an equilibrium mixture of the two. Hantzch and Kalb (*loc. cit.*) represent cotarnine cyanide as a derivative of the carbinol form (V).

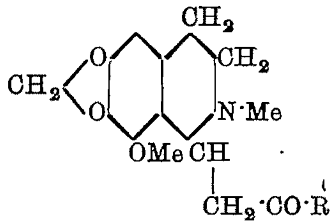
Freund and Becker (*Ber.*, 1903, **36**, 1521) who obtained *nor*cotarnine by the decomposition of cotarnine anilmethiodide, considered the reaction to be explained best by assuming the aldehyde constitution for cotarnine, while Liebermann, Kropf and Glawe (*Ber.*, 1904, **37**, 211, 2738) have suggested two alternative structures (VI and VII), derived from either the aldehydic or carbinol forms, for the products obtained by condensing cotarnine with ketones and ketonic bodies containing the $-CH_2 \cdot CO-$ grouping, thus:—



(V)

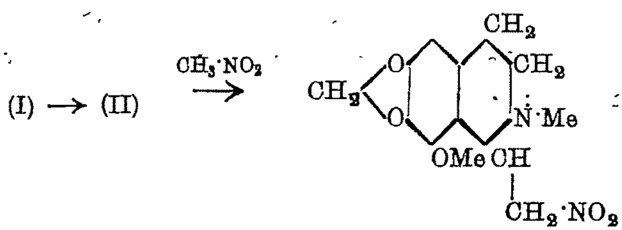


(VI)



(VII)

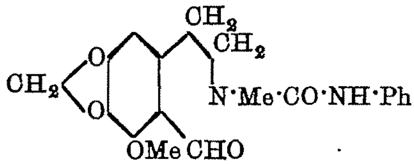
Hope and Robinson (*J. Chem. Soc.*, 1911, **99**, 1168; 2114) and Robinson and Robinson (*ibid.*, 1913, **103**, 372; 1914, **105**, 1456) who have studied the reaction between cotarnine and nitromethane and also between cotarnine and aromatic nitro bodies containing a reactive methylene group, have assigned the closed ring formulæ to the products and expressed the view that cotarnine existed normally in the aldehydic form which changed during the reaction into the carbinol form, a molecule of water being subsequently eliminated from the latter, thus:



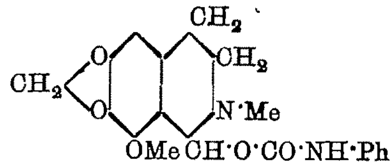
(VIII)

It seems clear, therefore, that the evidence on which the present conflicting views about the structure of cotarnine are based is far from satisfactory and the investigation of such reactions as might be interpreted without the least ambiguity in support of a definite constitution for this base would be desirable. In the present communication we have examined very fully the reactions of cotarnine with phenyl *iso*cyanate and phenyl *iso*thiocyanate and the results of our investigation have furnished a convincing proof of the aldehydic structure for this base.

The reactions which occur at the ordinary temperature and with quantitative yields of products may be expected to give rise to either a urea or a urethane derivative, according as we accept structures (I) or (II) for cotarnine, thus:—

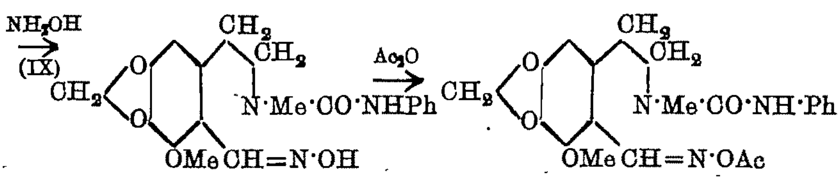


(IX)

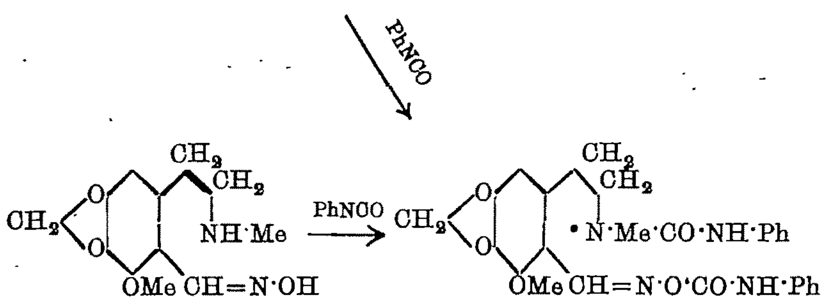


(X)

That the urea constitution (IX) is the only one that is tenable would be obvious from the following considerations: (*i*) it is completely insoluble in dilute acids which could hardly have been the case with a compound of the urethane structure in which the basic -N·Me- group remains free; (*ii*) it reacts smoothly with hydroxylamine to form a crystalline monoxime showing the presence of a free aldehyde group. The oxime is quite stable, dissolves unchanged in cold alkalis and is readily acetylated and benzoylated giving monoacyl derivatives which are insoluble in alkali. Moreover, the oxime is found to react again with phenyl *iso*cyanate to form the urethanourea derivative (XIII), the oximinohydroxyl group being evidently involved in the reaction. The same compound has been synthesised from cotarnine oxime and phenyl *iso*cyanate, the various reactions being explained by the scheme given below:—

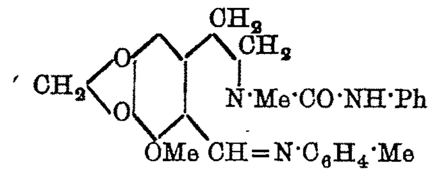


(XI) (XII)



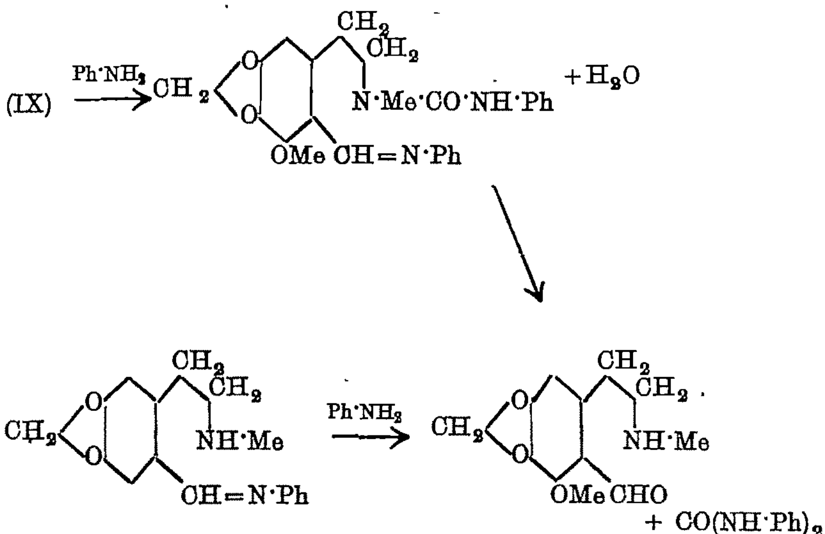
(XIII)

Fresh evidence of the existence of a free aldehyde group in cotarnomethylphenylurea is derived from its reaction with the toluidines (*o*-, *m*- and *p*-) which condense, on gently warming the components, to crystalline toluidils of the following type:—



(XIV)

The curious observation was made that when the same reaction was carried out with aniline, carbanilide was the only product that could be isolated. The reaction presumably takes place according to the following scheme:



(Cotarnine-anil)

The series of reactions mentioned above has also been carried out with phenyl *iso*thiocyanate, the resulting cotarnomethylphenylthiourea and its derivatives being similar in all respects to the simple ureas.

Should cotarnine have the carbinol formula it is difficult to conceive of any valid reason why the alcoholic group should not have reacted immediately to produce non-aldehydic urethanes differing fundamentally in their chemical behaviour from the aldehydic ureas

which were actually obtained. It seems to us that the reactions of cotarnine with phenyl *iso*cyanate and phenyl *iso*thiocyanate do not admit of any other interpretations than those given above and they constitute, therefore, fresh and clear evidence in favour of the aldehyde-imine structure for this base.

EXPERIMENTAL.

Cotarnomethylphenylurea (IX).—Cotarnine (2 g.) which has been freshly prepared, dried and powdered was suspended in dry benzene (12 c.c.) and phenyl *iso*cyanate (2 c. c.) quickly added and the mixture shaken. The mixture momentarily became clear and immediately after crystals of the new product began to separate. These were collected, washed thrice with small quantities of cold benzene and dried in the desiccator. It forms colourless rectangular prisms melting sharply at 137°, yield 2·4 g. It is perfectly insoluble in dilute hydrochloric acid, cold or warm. (Found: C, 63·6 ; H, 5·6 ; N, 7·96. $C_{19}H_{20}O_5N_2$ requires C, 64·0 ; H, 5·6 ; N, 7·86 per cent).

The *oxime* (XI).—The powdered urea (1·6 g.) was suspended in dry alcohol (10 c. c.), warmed to 50° and quickly treated with a solution of hydroxylamine hydrochloride (0·6 g.) and crystallised sodium acetate (1·6 g.) in 4 c. c. water. On stirring for a few minutes crystals of the oxime separated in glistening colourless plates, m. p. 152° (decomp.), yield 1·7 g. It dissolves slowly in cold caustic soda with a pale yellow colour and is reprecipitated unchanged on the addition of acids or passing CO_2 into the solution. (Found: C, 60 9; H, 5·48 ; N, 11·14. $C_{19}H_{21}O_5N_3$ requires C, 61·46 ; H, 5·66 ; N, 11·32 per cent).

Action of phenyl isocyanate *on the oxime of cotarnomethylphenylurea: Phenylurethane of cotarnomethylphenylurea oxime* (XIII).—The oxime (0·6 g.) was suspended in dry benzene (10 c. c.), phenyl *iso*cyanate (1 c. c.) added and the mixture warmed on the water-bath to about 50°, when the flask was soon filled with crystals. Crystallisation from hot alcohol gave colourless plates, m. p. 151°. The same compound was obtained in almost theoretical yield when cotarnine oxime, suspended in dry benzene, was treated with phenyl*iso*cyanate, m. p. 151°, proved to be identical with the previous compound by a mixed m. p. (Found: C, 63·2 ; H, 5·2 ; N, 11·62. $C_{26}H_{26}O_6N_4$ requires C, 63·7 ; H, 5·3 ; N, 11·43 per cent).

Acetylation of the oxime of cotarnomethylphenylurea (XII).—The oxime (0·6 g.) was treated with 10 drops of freshly distilled acetic anhydride and gently warmed on the water-bath until there was a clear yellow solution. The cold solution was rubbed with a few drops of 2*N*-alkali and the separating granular solid washed with water and crystallised from dilute alcohol as colourless prismatic needles, m. p. 189°. (Found: C, 61·2 ; H, 5·5 ; N, 10·15. $C_{21}H_{23}O_6N_3$ requires C, 61·0 ; H, 5·57 ; N, 10·17 per cent).

Benzoylation of the oxime of cotarnomethylphenylurea.—The oxime (1 g.) was dissolved in excess of 2*N*-alkali and the solution rubbed vigorously in a mortar with 1 c. c. of benzoyl chloride until the oil completely solidified. After washing with alkali and crystallising from alcohol it was obtained in long colourless plates, m. p. 142°. (Found: N, 8·88. $C_{26}H_{25}O_6N_3$ requires N, 8·82 per cent.).

Condensation of Cotarnomethylphenylurea with Aromatic Amines.

(*a*) *Aniline.*—The urea (1 g.) was mixed with freshly distilled aniline (2 c. c.) and stirred until it dissolved. On keeping the solution overnight at room temperature needle-shaped crystals were found to be deposited which were identified as carbanilide (m. p. 238°) by m. p. and mixed m. p. determination.

(*b*) p-*Toluidine.*—Molecular quantities were dissolved in the minimum amount of alcohol, mixed and warmed gently and allowed to stand overnight. The solid, which separated, crystallised from hot alcohol in colourless needles which changed colour at 186° and melted at 168°. (Found: N, 9·62. $C_{26}H_{27}O_4N_3$ requires N, 9·43 per cent).

(*c*) o-*Toluidine.*—The oil, which separated on diluting the alcoholic solution, was treated with dilute acetic acid when it solidified. Crystallisation from alcohol gave small colourless needles, m. p. 196°. (Found:, N, 9·58. $C_{26}H_{27}O_4N_3$requires N, 9·43 per cent).

(*d*) m-*Toluidine.*—The product was obtained in the same way as that from *o*-toluidine. Long prismatic needles, m. p. 168°. (Found: N, 9·7. $C_{26}H_{27}O_4N_3$ requires N, 9·43 per cent).

Action of phenyl iso*thiocyanate on cotarnine*: *cotarnomethylphenylthiourea.*—Finely powdered cotarnine (1 g.), suspended in dry benzene (8 c. c.), was treated with phenyl *iso*thiocyanate (1 c. c.) and the mixture stirred and warmed until a clear solution was obtained. On cooling in ice the thiourea separated out quantitatively in shining crystals from excess of hot benzene as flat needles, m. p. 132°,

depressed by admixture with cotarnine to 116°. It is completely insoluble in cold dilute acids. (Found: C, 61·68; H, 5·5 ; N, 7·8. $C_{19}H_{20}O_4N_2S$ requires C, 61·8 ; H, 5·4 ; N, 7·5 per cent).

The *oxime* was prepared in precisely the same way as the urea oxime. It crystallised from alcohol in lustrous rhombic plates, m. p. 142°. It dissolves in dilute caustic soda only on warming and is reprecipitated on acidification. (Found: N, 10·9. $C_{19}H_{21}O_4N_3S$ requires N, 10·85 per cent). The hydroxyl group of the oxime is apparently non-reactive towards phenyl *iso*thiocyanate, for neither the urea nor the thiourea oximes could be made to condense with this reagent to form the desired urethane derivatives, only unchanged material being recovered at the end.

The *acetyl* derivative of the thiourea oxime, prepared in the usual way, crystallises from alcohol in stellate clusters of needles, m. p. 147°, insoluble in alkali. (Found: N, 9·89. $C_{21}H_{23}O_5N_3S$ requires N, 9·79 per cent).

The *benzoyl* derivative crystallises from a large excess of boiling alcohol in thin plates, m. p. 158°. (Found: N, 8·7. $C_{26}H_{25}O_5N_3S$ requires, N, 8·55 per cent).

Cotarnomethylphenylthiourea anil.—The clear solution, obtained on mixing molecular proportions of aniline and the thiourea and warming to 40° on the water-bath, was cooled and treated with a few drops of dilute acetic acid and rubbed vigorously. The oily product soon solidified and was washed with alcohol and crystallised from a mixture of benzene and petroleum ether as needles, m. p. 146°, mixed with thiocarbanilide the m. p. was depressed to 130°. (Found: N, 9·2. $C_{25}H_{25}O_3N_3S$ requires N, 9·39 per cent).

We desire to express our thanks to the Superintendent of the Govt. Opium Factory at Ghazipur for a kind gift of pure narcotine which was used in this investigation.

PRESIDENCY COLLEGE,
MADRAS.

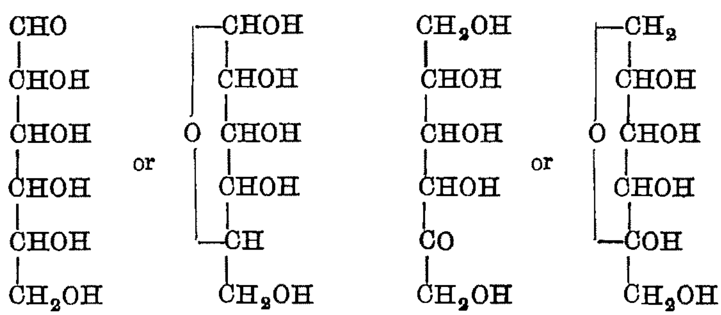
Received May 26, 1934.

Parachor and Chemical Constitution. Part I. Structure of the Carbohydrates.

By Susil Kumar Ray.

According to the modern conception of the structure of sugars as established by the work of Haworth and his collaborators (Haworth, "Constitution of Sugars," 1929) these bodies are represented as having an oxygen ring, but nevertheless owing to the ready reducing properties of the sugars it is admitted that this structure is anything but stable. The object of the present paper is to find out which of the following two structures agrees with the parachor contribution of the sugar molecule.

Glucose Fructose



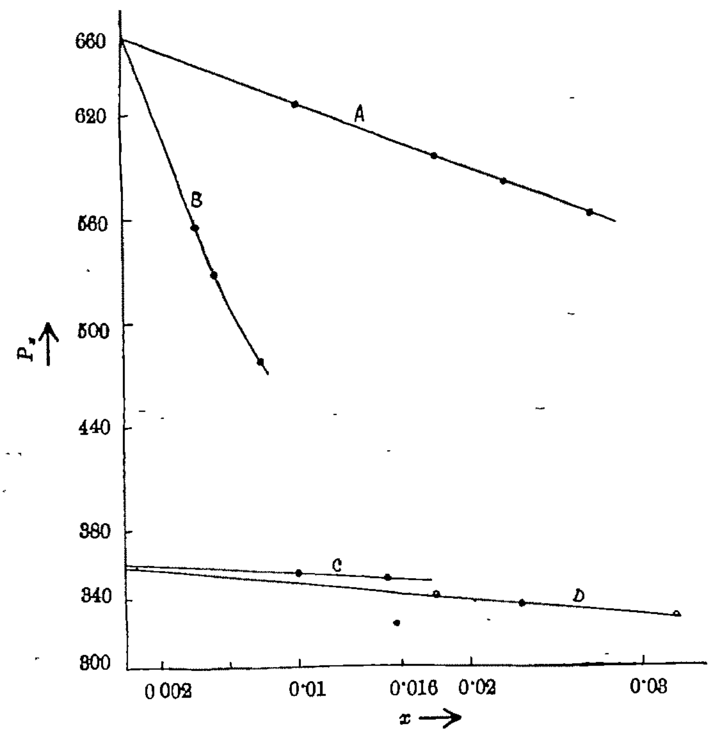
($P=377·2$) ($P=360·1$) ($P=377·2$) ($P=360·1$)

Two monosaccharoses, glucose and fructose and two disaccharoses, sucrose and maltose were investigated. The surface tension was determined by the method of maximum bubble pressure; the apparatus employed was of the usual Sugden type. The determination of surface tension in the fused condition, except in the case of fructose, was found to be extremely difficult as the sugars rapidly become brown on prolonged heating. Hence the determinations were made very quickly.

The surface tension of maltose in the fused state cannot be determined as it decomposes immediately on fusion. To obviate this difficulty the penta-acetyl derivative of glucose and the octa-acetyl derivatives of sucrose and maltose were also examined as they are found to be more stable. The densities were determined by means of a **U**-shaped pyknometer. It will be seen from the results that the parachor contribution agrees very closely with the oxide ring structure

as proposed by Haworth and his collaborators. Thus it can be definitely said that in the fused state sugar molecules exist as ring compounds.

The density and surface tension were determined also in solution and the parachor calculated from the results obtained (*cf.* Ray, *J. Indian Chem. Soc.*, 1934, 11, 671). The solvents employed were water and pyridine, the only two liquids in which the sugars were found to be fairly soluble. It will be seen that in the aqueous solutions normal results were obtained in very dilute solutions. With increase of concentration, after a certain limit, the parachor was found to diminish. In pyridine the values were never normal. With decreasing concentration of the sugars, the parachor increases rapidly and approaches the normal value. By plotting x against P_x, a curve is obtained which was found to intersect the P_x axis at the required value.



A, B, C and D refer to maltose, sucrose, glucose and fructose respectively.

These results will be evident from the curves given above. In this connection it is to be noted that similar results were obtained by Hammick and Andrew (*J. Chem. Soc.*, 1929, 754) with some liquid mixtures but their results were found to increase with increasing concentration.

TABLE I.

Parachor in fused state.

Carbohydrates.	Temp.	Density.	Surface tension.	Found P.	Calculated. P_{ring}.	P_{open}.
Fructose	100°	1·459	72·83	360·6	360·1	377·2
	180°	1·435	68·64	360·8	360·1	377·2
Glucose	170°	1·461	71·73	358·8	360·1	377·2
Sucrose	170°	1·429	62·20	672·0	668·4	...
Penta-acetyl-glucose	150°	1·141	25·96	771·5	779·1	796·2
Octa-acetyl-sucrose	78°	1·257	36·91	1331	1339	...
Octa-acetyl-maltose	170°	1·185	30·04	1339	1336	...

In Table II, x is the molar fraction of the solute, M_m the mean molecular weight of the solution, P_m the mean parachor and P_x the parachor of the solute. The observations were carried out at the temperature of about 32°.

Parachor in Solution.

TABLE II.

Glucose in water.

x.	Density.	M_m.	Surface tension.	P_m.	P_x.
0·0	0·9967	18	70·59	52·34	...
·006582	1·0209	19·08	71·60	54·37	361·4
·007741	1·0254	19·25	72·04	54·71	359·1
·01196	1·0409	19·93	72·21	55·82	348·6
·01556	1·0547	20·52	72·91	56·82	340·6

Fructose in water.

0·004930	1·0166	18·81	71·78	53·84	359·2
·008796	1·0297	19·42	72·58	55·04	359·3
·01203	1·0424	19·95	72·73	55·91	349·1
·01428	1·0500	20·31	72·70	56·48	343·2

Sucrose in water.

x.	Dens.	M_m.	Surface tension.	P_m.	P_x.
0·003629	1·0236	19·18	71·98	54·53	666·8
·006229	1·0423	19·55	72·86	54·80	666·2
·007638	1·0504	20·47	73·10	57·01	663·7
·01000	1·0684	21·24	73·41	58·24	642·2

Maltose in water.

x.	Dens.	M_m.	Surface tension.	P_m.	P_x.
0·002098	1·0118	18·69	71·13	53·63	667·3
·003999	1·0238	19·30	71·45	54·80	667·9
·005448	1·0340	19·77	71·96	55·68	664·5
·008640	1·0534	20·79	72·18	57·55	655·1

In Table III, the figures within parentheses are obtained from the curves given above.

TABLE III.

Glucose in pyridine.

x.	Density.	M	Surface tension.	P_m.	P_x.
0·0	0·9734	79	35·32	197·7	...
·01153	0·9830	80·17	35·72	199·5	355·4
·01536	0·9879	89·54	35·74	200·0	351·9
1·0	...	...	...	...	(360·0)

Fructose in pyridine.

x.	Density.	M	Surface tension.	P_m.	P_x.
0·01806	0·9889	80·82	35·91	200·8	342·6
·02507	0·9941	81·53	36·16	201·2	335·1
·03217	1·0006	82·24	36·46	202·0	329·6
·06503	1·0301	85·56	37·61	205·7	321·4
1·0	...	...	...	...	(358·0)

Sucrose in pyridine.

x.	Density.	M	Surface tension.	P_m.	P_x.
0·004318	0·9799	80·13	35·21	199·2	555·8
·005301	0·9809	80·38	35·63	200·2	528·3
·008160	0·9857	81·13	35·19	200·8	477·9
1·0	...	...	...	...	(664·0)

Maltose in pyridine.

x.	Density.	Surface tension.	M_m.	P_m.	P_x.
0·01020	0·9908	81·69	86·08	202·1	625·0
·01854	1·0020	83·87	86·04	205·0	593·3
·02252	1·0102	84·91	86·15	208·2	577·3
·02685	1·0175	86·06	86·24	207·4	558·8
1·0	...	...	...	...	(663·0)

Summary.

The surface tension and density of glucose, fructose, sucrose and maltose were determined in the fused state as well as in solution and the parachor calculated. The parachor values were found to agree with the ring structures as proposed by Haworth and his collaborators.

My grateful thanks are due to Prof. P. R. Rây of the University College of Science and Prof. A. Maitra of the Presidency College for the kind interest they took in the work.

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Review.

An Introduction to the Biochemistry of Nitrogen Conservation by Dr. Gilbert J. Fowler. Published by E. Arnold & Co., London, 1984. Pp. 280 + viii.

Professor Fowler has described in a lucid manner in this book his life's work on the problem of the supply of combined nitrogen cheaply. He has dwelt at length on the various processes for the utilisation of the combined nitrogen in plant leaves and residues, sewage water, night soil and other waste products. The author's work on sewage disposal by the " activated sludge " method is very important and his processes are being utilised by many big cities. He has discussed the subject satisfactorily from a bacteriological chemists' view point and has explained clearly the various processes involved in the transformation of the proteins present in the waste products to nitrites and nitrates, which serve as plant food. As is expected, the part played by the physical factors, *e. g.*, light, increase of temperature, etc., in the processes of ammonification, nitrification and nitrogen fixation has not yet been properly valued—there is no doubt that these factors assume important proportion in these processes especially in tropical places. A type of denitrification taking place in the presence of oxygen, first observed by Lipman and Blair and emphasised by Russell and recently explained, involving a loss of as much as 100 lbs. nitrogen per acre of soil annually has not been mentioned in this book.

This publication is an important contribution to the problem of nitrogen conservation, which is of vital importance all over the world, specially in poorer countries and this volume should be not only in the possession of all chemical libraries but also in the hands of persons wishing the agricultural prosperity of their country.

N. R D.

Cellulose Fermenters from Horse-dung.

By H. K. Sen and Gopal Chandra Das-Gupta.

The discovery of any suitable type or types of bacteria that would easily ferment cellulose is important for the practical utilisation of waste plant materials. Till lately, no bacteria were isolated which could carry on cellulose fermentation to such an extent and with such rapidity that the possibility of their industrial use could be thought of in the near future. The case of sewage bacteria which are made use of in isolated instances in the activated sludge processes is, however, different, as the nature of the liquor to be fermented there is complex and not typical of the kind of liquor usually available in cellulose fermentation. The economics of the activated sludge process have been questioned here and there, but the uniformity and the certainty which have been by now realised in sludge digestion, leave no doubt that as soon as a profitable use for methane is found, the process will have taken its place of importance. The bulkiness of the sludge digestion process and the comparatively long time required for the fermentation of resistant celluloses make the introduction of cellulosic matters from outside for the purpose of increased fermentation, impracticable. Hence, the treatment of cellulosic or lignocellulosic matters by chemical processes to convert them quickly into industrial products, with comparatively lesser outlay has had always a great attraction.

We had, therefore, undertaken laboratory investigation on the decomposition of cellulose by means of bacteria. Suitable types of bacteria cannot be said to have been isolated, although several mixed types carry on the degradation of cellulose under thermophilic conditions far enough to be technically promising. The products obtained by such bacterial fermentations are varied, but these could be grouped under two heads :—(*i*) Liquid products consisting of formic, acetic and butyric acids and alcohol and (*ii*) gaseous products consisting under usual circumstances, of methane, hydrogen and carbon dioxide, and under special circumstances, only carbon dioxide. The earliest researches on the fermentation of cellulose under anaerobic, mesophilic conditions were by Omeliansky (1895-1902), who isolated in more or less pure

condition, methane-fermenting and hydrogen-fermenting bacteria from the mud of the river Neva. But the credit of perceiving the importance of the action of thermophilic organisms on cellulose may be given to Macfadyen and Blaxall (*Trans. Inst. Preventive Medicine*, 1899, p. 162), who obtained enrichment cultures from stable manure capable of fermenting cellulose. Pringsheim (*Centr. Bakt. Abt.*, 1912, **38**, 2) described a cellulose-destroying enzyme in a culture fermenting at 55°. He made further the very important observation that in the fermentation of cellulose, cellobiose and glucose are intermediate products. The qualitative nature of the products of cellulose fermentation is alike, as noticed by both sets of workers, acetic and formic acids being noticed by both of them. Thereafter, thermophilic cellulose fermenters were recognised to be fairly widely distributed in nature. Kroulik in 1918 described four species—3 plectridia and 1 with a central spore, 2 being aerobic, and 2 anaerobic. He was of the opinion that the two aerobic organisms which were abundant during the early stages of the fermentation were not cellulose fermenters, because when isolated on beef extract agar plates, they showed no activity. The anaerobic organisms did not grow on agar, thus showing an important distinction between the two. He found some of these cultures resistant to the action of steam and the production of acetic, butyric, formic and lactic acids was also noticed. The gases that evolved were found by him to be carbon dioxide and hydrogen. In any case, he failed to isolate pure cultures. Langwell and Lymn (*J. Soc. Chem. Ind.*, 1923, **42**, 280 T) published some interesting results on the fermentation of cellulose by thermophilic bacteria isolated from fermenting horse manure. It is claimed that large amounts of sulphite pulp were readily fermented with the production of acetic, butyric and lactic acids, ethyl alcohol, methane, hydrogen and carbon dioxide. These results have been d-ubted by some authorities and a detailed confirmatory report by the author would be extremely welcome on this very important work. Khouvine (*Ann. de l° Inst. Pasteur*, 1923, **37**, 711) described an organism isolated from human faeces which was exclusively a cellulose fermenter, working at 35·51°, the main products of the fermentation were acetic acid, ethyl alcohol, carbon dioxide and small amounts of butyric acid and hydrogen. There was no distinct optimum temperature for the action of this organism and fermentation began only when some sterilised faecal extracts were added to the medium.

Neuberg and Cohn (*Biochem. Z.*, 1923, **139**, 527) obtained from canal mud and horse manure enrichment cultures capable of fermenting cellulose at 53-55°. Viljoen, Fred and Peterson (*J. Agric. Science*, 1926, **16**, 1) claim to have isolated a type of thermophilic cellulose fermenter in a pure condition from an infusion of 100 g. of a rapidly fermenting manure in 200 c.c. of water. Thaysen has doubted the purity of the bacterium isolated by the authors since they obtained the culture they describe as pure from a dilution containing as much as one ten-thousandth part of the crude culture, and from this dilution in cellulose agar they isolated not one well-circumscribed colony, but were content to employ as inoculant for their pure cultures a part of this agar medium containing a gas bubble. Even starting with a culture that is only slightly infected, it is highly improbable that the above procedure could lead to the isolation of pure cultures (*cf.* Thaysen and Bunker, "The Microbiology of Cellulose, Hemicellulose, Pectins and Gums," p. 61).

Macfayden and Blaxall (*loc. cit.*) thought that the fermentation was brought about by the combined action of symbiotic strains. Our present work seems to support this observation of Macfayden and Blaxall. We have started with horse-dung and been able to isolate two strains of bacteria which are weak cellulose fermenters separately, but which, when brought together, in the medium for cellulose fermentation, are capable of fermenting the cellulose under favourable circumstances, almost completely. Generally, however, a conversion of 50 to 60% of the cellulose is reached, the liquid products being acetic, formic and butyric acids and alcohol, and the gaseous product carbon dioxide, a large proportion of which is derived from the neutralisation of calcium carbonate by the produced acid. The activity of the two bacteria towards cellulose continues to diminish, till after six months, they showed very reduced function. To sugars and starches, however, they retained the usual initial activity. No explanation has yet been found for this deterioration, nor any specific means of reactivation. It should be noticed here that a large quantity of sulphuretted hydrogen, specially in the beginning of fermentation, is noticed, derived no doubt from the nutrient substances added to the medium. This symbiotic action is still more energetic in less purified enrichment cultures, a fact which would indicate that although some cellulose-fermenters *per se* have been isolated, for technical degradation of cellulose, the symbiosis of more numerous types of bacteria is probably essential. If one disallows the purity of Viljoen-Fred-Peterson's bacterium as suggested by

Thaysen, the mechanism of the fermentation of cellulose in their case can also be considered to be due to symbiosis. In the case of the two types isolated by us, there is no inability on the part of either to ferment starch, sugars (hexoses and pentoses) or hemicelluloses. If we admit that in the degradation of cellulose, cellobiose and glucose are obligatory intermediates, then it is difficult to reconcile the behaviour of Madame Khouvine's organism or that of Hutchinson and Clayton's *Spirochaeta Cytophaga*, which are both characterised by their unique inability to ferment carbohydrates except cellulose.

So far, the only large scale experiments on the fermentation of cellulose on record are those by Fowler and Joshi (*J. Ind. Inst. Sci.*, 1920, **3**, 39), and the one described by Langwell and Lymn (*loc. cit.*). The observation of Fowler and Joshi that hemicelluloses were more suitable for fermentation than the more resistant celluloses, reduces the usefulness of their bacteria, no pure culture of which is on record. Tomoda (*J. Soc. Chem. Ind*, *Japan*, 1932, **35**, 584B) who appears to have isolated a species of *Clostridium thermocellum* as described by Viljoen, Fred and Peterson (*loc. cit.*) in determining mechanism of the decomposition of cellulose fibre by the action of microorganisms opines that this mechanism is quite different from that of the hydrolysis of cellulose or cellulose solution by acids. It would be important to reconcile this hypothesis with that of Pringsheim who regards cellobiose and glucose as the intermediates.

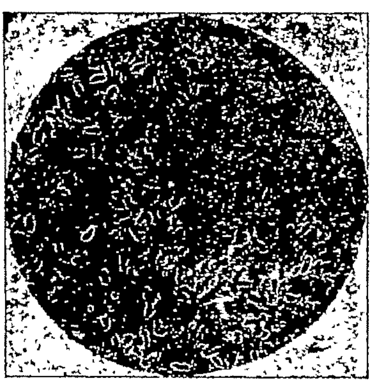
Method of isolation of the two types of cellulose fermenting bacteria.—2 G. of sun-dried horse-dung were kept in a watch glass for 4 hours at 55° to eliminate mesophilic organisms. The substance was then added to an enrichment medium of the following composition:

Dipotassium phosphate ...	0·1 g.	Potassium nitrate ...	0·2 g.
Magnesium sulphate ...	0·1	Strips of filter-paper ...	2·0
Sodium chloride ...	0·1	Water ...	100 c. c.
Calcium carbonate ...	0·2	p_H adjusted to 7·4	

The whole was then heated on the water-bath for 10 minutes at about 75-80° and then incubated at 55° for about 5 days, when the filter paper was found to have commenced disintegrating. In 10 days' time the disintegration was practically complete, evolution of gas (methane, hydrogen and carbon dioxide) being noticed all the time. A portion of the disintegrated but still fibrous mass of the filter-paper was taken out by a platinum loop and introduced into 5 c. c. of sterile

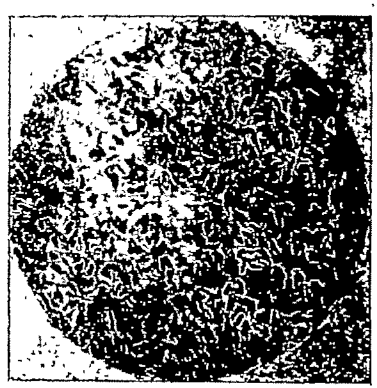
physiological solution (0·85% sodium chloride solution in distilled water) containing a few glass beads, in a test tube. The mass was thoroughly shaken, and 1 c. c. of it was added to a second lot (100 c. c) of the enrichment medium and allowed to be incubated. After 4 days, a third enrichment was effected. From this actively fermenting enrichment. plating was done, the medium for plating being composed of trypsin-digested casein (100 c. c), distilled water (850 c. c.), beef extract (1 g.), agar (30 g.), filter paper (finely subdivided) 10 g. and p_H 7·4. Starch-agar, glucose-agar and nutrient-agar were also tried for plating, but with indifferent results.

After 24 hours of incubation at 55°, which is found to be the optimum temperature two types of colonies appeared, which were almost similar in size, but one was *creamy white*, and the other *grey*. The two types were separately plated, with the result, however, that both the creamy white and the grey types reappeared in each of the plates, with this distinction that the number of grey colonies was disproportionately large in comparison with the creamy white ones. At first, the grey colonies being predominant, further purification of this type was effected by several platings (five times usually). Below is a micro-photograph of this type with a magnification of 1 × 1200.



TYPE I.

Stained with carbinol fuchsin for 30″—24 hours' growth.



TYPE II.

Stained with carbinol fuchsin 30″—24 hours' growth.

The action of this type on cellulose was very weak, a disappearance of 15-20% of the cellulose taken for fermentation being noticed at the

end of 7 days. This led to the suspicion that perhaps the type of organism having the creamy white colony might be responsible for the active fermentation of cellulose. Hence, this latter type was purified by repeated plating with the same medium and its action on cellulose investigated.

There was practically no action of the second type on cellulose. Both these isolated types, however, are capable of fermenting hemicelluloses, pentoses, sugars and starch, a fact which distinguishes them from Madame Khouvine's and Hutchinson and Clayton's organisms which can act only upon cellulose and on no other carbohydrate.

The qualitative nature of the gaseous products from the action of our bacteria on cellulose requires special mention. So far, all the organisms described give rise to methane, hydrogen and carbon dioxide in the impure stage, *i.e.*, in the enrichment stage, all those gases were found to be present. After purification by plating, neither hydrogen nor methane is evolved, the sole gaseous products being carbon dioxide and sulphuretted hydrogen. The latter no doubt is derived from medium.

* TABLE I.

Carbohydrate fermented.	Analyses of gases produced by the first type of bacterium.				
Arabinose	CO_2	5·14%	4·5%	4·5%	5·0%
	CH_4	...	...	...	...
	H_2	...	...	...	...
Xylose	CO_2	7·0	5·2	4·5	8 9
	CH_4	...	...	...	...
	H_2	...	...	...	...
Starch	CO_2	3·65	4·5	3·4	7·9
	CH_4	...	...	...	...
	H_2	...	...	...	...
Molasses	CO_2	32 2	39·0	52·0	...
	CH_4	...	...	...	...
	H_2	50·0	48·0	30·0	...

* The fermentation of molasses is characterised by the evolution of hydrogen, which is absent in other fermentations. In all these analyses, the residue was composed of nitrogen, oxygen and sulphuretted hydrogen in varying proportions. The second type of bacterium yielded similar results.

So far as the liquid products are concerned, there is no essential qualitative difference, acetic, formic and butyric acids in the main as also a certain percentage of ethyl alcohol being produced.

The following table shows the difference or otherwise of the analogous bacteria.

TABLE II.

Comparison of certain thermophilic cellulose fermenting bacteria.

	Langwell.	Fred. Peterson and Viljoen.	Sen and Das-Gupta. Type I.	Type II.
Size of rods.	4 × 0·4 μ	5 × 0·4 μ	× 0·75 − 1·0 μ	2 × 0·5 μ
Size of spore.	Not given	0·9 × 0·6 μ	2 × 1·0 μ	2 × 1·0 − 1·25 μ
Flagella.	Absent.	Peritrichous.	Absent.	Absent.
Gram-stain.	Negative.	Negative.	Negative.	Negative.
N. Broth with glucose.	Gas and acid.	Gas and acid.	Gas and acid. (sediment).	Gas and acid. (surface growth).
N. Agar stroke.	Shining, moist, butyrous.	Shining, moist, butyrous.	Dull, dry, butyrous. (slightly spreading).	Dry, creamy, butyrous (not spreading).
Potato slant.	Yellow, moist, potato browned.	Yellow, potato browned.	Grey, dry.	Creamy, potato slightly darkened.
N. Agar plate.	Small surface & sub-surface colonies.	Small sub-surface colonies. Profuse growth on starch agar.	Scanty growth surface colonies slightly spreading.	Scanty growth small surface colonies (smaller than Type I).
Milk.	Acid, curdled in 5 days.	Slightly acid in 3 days.	Slightly acid in 3 days. (no curdling).	Slightly acid in 3 days. (no curdling).
Carbohydrates fermented.	Cellulose, starch hemicellulose, hexose & pentose, etc.	Cellulose, starch, hemicellulose, hexose & pentose, etc.	Hemicellulose, starch, hexose, pentose & cellulose slightly.	Hemicellulose, starch, hexose, pentose & cellulose slightly.

No liquefication of gelatine or detection of sugar as intermediate product; nor indole formation noticed.

From a perusal of the above table, the separate identity of these two types of bacteria can be inferred, the most characteristic feature being the increased activity on symbiosis.

TABLE III.

The action of Type I on xylose, arabinose, starch, cotton, glucose, filter paper, rice-straw, and water hyacinth:

Substance fermented.	Substance taken as reducing sugar.	Fermenting period.	0·1 N acid formed.	Acid formed (expressed as acetic acid).	Alcohol formed.	Residue.
Straw digested	5 g.	3 days	265·6 c.c.	31·8%	—	62·0%
	5	5	484·0	58·08	5·3%	32·6
	5	7	726·0	87·12	6·27	0·6
Arabinose	5	3	200·8	24·1	—	61·0
	5	5	661·6	79·39	—	17·4
	5	7	664·0	79·68	3·0	16·4
Glucose	5	3	229·0	27·48	6·21	64·8
	5	5	650·0	78·0	6·98	13·86
Xylose	5	5	754·4	90·53	3·85	0·32
Starch	5	5	776·18	93·14	3·2	1·6
Water hyacinth digested	5	7	—	—	15·23	1·98
	5	7	—	—	11·90	—
	5	7	—	—	12·96	2·25
	5	7	—	—	11·99	—
Molasses	5·85	5	540·78	55·5	13·68	29·95
	5·85	5	518·34	53·26	10·96	35·9
	3·45	5	374·50	64·4	23·8	12·35
	4·18	5	468·48	67·23	19·47	14·05

Each set of experiment is the average of five experiments.

The action of Type II on xylose, glucose and hyacinth, etc., will be understood from the following table.

TABLE IV.

Substance fermented.	Substance taken as reducing sugar.	Fermenting period.	0·1 N Acid formed.	Acid formed (expressed as acetic acid).	Alcohol formed.	Residue.
Xylose	5 g.	5 days	624·0 c.c.	74·88%	6·50%	18 6%
Glucose	5	5	508·0	60·90	5·60	33·8
Hyacinth	5	7	—	—	18·25	11·37
	5	7	—	—	15·12	13·25

A comparative chart on the action of bacteria Type I and Type II individually and mixed together on cellulose is givenbelow.

TABLE V.

Type I.			Type II.			Type I & II mixed together.		
Cellulose (filter paper)	Alcohol.	Acid (expressed as acetic).	Cellulose (filter paper)	Alcohol.	Acid. (acetic acid).	Cellulose (filter paper)	Alcohol.	Acid. (as acetic acid).
5g.	1·90%	18·26%	2g.	3·25%	13·56%	5g.	14·6%	66·87%
5	5·52	12·90	5	4·30	17·27	5	11·35	81·96
5	5·06	15·67	5	2·25	15·20	5	10·20	47·0

The effect of concentration of the sugar solution on the total fermentibility.—A 2% arabinose solution was fermented with the result that 26% sugar was left unacted, whilst the acid figure was 56·6 c.c. $N/10$ acid per g. of sugar. With a 1% arabinose solution the unacted sugar was 17% and the acid figure was 75 84 c.c. of $N/10$ acid.

The Influence of p_H Value of the Medium on Fermentibility.

$P_h = 6·6$	...	very slight growth.
$P_h = 7·0$	...	moderate growth.
$P_h = 7·4$	...	normal vigorous growth.

In the last instance, the p_H value decreased rapidly and soon reached a point (6·5 – 6·6) where activity was hampered by the slight acidity of the medium. 1% Calcium carbonate was, therefore, added to keep the p_H value steady between 7 and 7·4.

Influence of temperature.—At room temperature (28° – 32°), there was no fermentation, but the organism lives. The optimum temperature was found to be 55°. The spores can resist steam-temperature (100°) for 10 minutes.

Analysis of the total fatty acids obtained from the fermentation of filter paper, arabinose and glucose, the proportions being in each practically the same. Butyric acid, 30%; formic acid, 25%; acetic acid, 45%. The estimation of these acids was done according to the following method: The total acid was at first treated with a baryta water and the whole was evaporated to dryness on the water-bath. The residue was left in contact with absolute alcohol for 6 hours with occasional stirring. The soluble barium butyrate was separated by filtration, the alcohol evaporated on the water-bath and the butyric acid liberated by the addition of dilute sulphuric acid, distilled in steam and titrated. The residue left after extraction of barium butyrate, was steam-distilled in the presence of phosphoric acid. The distillate was treated with magnesium sulphate and evaporated to dryness. The dried mass was again extracted with absolute alcohol, when magnessium acetate went into solution. The solution was evaporated and the acetic acid liberated by dilute sulphuric acid as before and steam-distilled and estimated by titration. Similarly, formic acid remaining in the residue was estimated.

Estimation of alcohol.—10-12 G. of potassium dichromate were dissolved in water and 30-35 c.c. concentrated sulphuric acid were added to it. This mixture was used for oxidising the alcohol obtained in the distillate from the fermented liquor. This distillate amounted usually to 500 c.c., which was kept in contact with the oxidising mixture for 20 minutes and was then steam-distilled and the acetic acid was estimated.* It should be noted that perceptible quantities of butyric acid or even butyraldehyde were present in this distillate,

* The distillation was continued till a few drops of the distillate showed an exceedingly weak test for acid with blue litmus paper. The total distillate was titrated against $N/5$ alkali, and the result expressed in term of ethyl alcohol, *assuming the whole of the acid to be acetic acid.*

proving the presence of butyl alcohol in the fermentation process. This method, which is a shortened form of Docks and Lamb's process, gave good results. Experiments with absolute alcohol agreed up to 97% usually.

Our thanks are due to Messrs. Radhanath Chatterjee, M.Sc., and Birendranath Majumdar, M.Sc., who have rendered considerable help in carrying out some of the duplicate experiments, as also generally.

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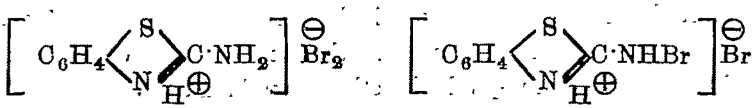
The Formation and Stability of Polybromide Derivatives of Heterocyclic Compounds. Part IV. The Hydrodibromides and Hydrotetrabromides of some 1-Dimethylaminobenzthiazoles.

By Mohammad Waheed Bukhsh, Ranchhodji Dajibhai Desai and Robert Fergus Hunter.

Since 1-aminobenzthiazole hydrodibromide (Hunter, *J. Chem. Soc.*, 1930, 125) fails to exhibit the paramagnetism to be anticipated on the basis of the odd-electron structure (I) (Aliazam, Hunter and Khan, *J. Chem. Soc.*, 1934, 708), it has been suggested to us that the compound may possess a nitrogen bromide structure of the type (II).



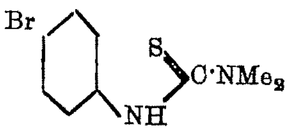
(I) (II)

This formula is, however, quite inadmissible in the light of the behaviour of the substance on pyrolysis and the total absence of evidence of any substitution during its preparation from the hydrobromic acid salt of 1-aminobenzthiazole and bromine (Hunter, *loc. cit.*). Nevertheless, in view of this suggestion, it appeared of interest to re-examine the dibromide of 1-dimethylaminobenzthiazole obtained from *s*-phenyldimethylthiocarbamide and bromine some years ago (Hunter and Styles, *J. Chem. Soc.*, 1927, 1209), in which the possibility of substitution by bromine in the μ-amino group is definitely precluded.

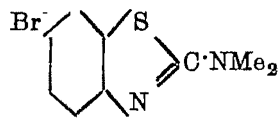
As might be anticipated, the supposed dibromide is actually a hydrodibromide of the dimethylamino base, analogous to the bromo-addition compound of 1-aminobenzthiazole obtained from phenylthiocarbamide under similar conditions (*cf.* Dyson, Hunter, Jones and Styles, *J. Indian Chem. Soc.*, 1931, 8, 147).

On more prolonged bromination in presence of excess of the

halogen, *s*-phenyldimethylthiocarbamide gave rise to a hydrotetrabromide of a monobromo base which yielded 6-bromo-1-dimethylaminobenzthiazole (IV), whose constitution was established by synthesis from *s*-*p*-bromophenyldimethylthiocarbamide (III), on treatment with sulphurous acid (*cf.* Chowdhury, Desai, and Hunter, *Rec. trav. chim.*, 1934 **53**, 1).

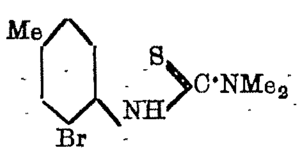


(III)

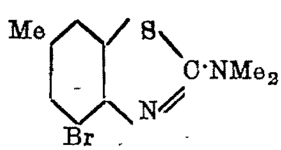


(IV)

A similar hydrodibromide of 1-dimethylamino-5-methylbenzthiazole was also obtained from *s*-*p*-tolyldimethylthiocarbamide, by treatment with bromine under conditions similar to those employed in the case of the phenyl derivative. On more prolonged treatment with excess of bromine, the cyclised product underwent nuclear substitution as in the case already described, yielding a hydrotetrabromide of a base identical with 3-bromo-1-dimethylamino-5-methylbenzthiazole (VI) obtained by cyclisation of *s*-*o*-bromo-*p*-tolyldimethylthiocarbamide (V).



(V)



(VI)

Since the formation of hydrodibromides and hydrotetrabromides of aminobenzthiazole bases is no longer explainable on the basis of the existence of even-numbered polybromide ions (*cf.* Dyson, Hunter, Jones and Styles, *loc. cit.*), it appears highly probable that these compounds are complexes of the type $\left[\text{Base}, \overset{\oplus}{\text{H}}\right]_2 \overset{\ominus}{\text{Br}}\ \text{Br}_2\ \overset{\ominus}{\text{Br}}$ and

$$\left[\text{Base}, \overset{\oplus}{\text{H}}\right]_2 \overset{\ominus}{\text{Br}}\ (\text{Br}_2)_3\ \overset{\ominus}{\text{Br}}$$ respectively.

Experimental.

s-Phenyldimethylthiocarbamide, prepared by treating a solution of phenylthiocarbimide (5 g.) in benzene (25 c.c.) with a 33 % solution of dimethylamine in alcohol (6 c.c.) and heating the mixture, crystallised in needles, m.p. 133° (Dixon, *J. Chem. Soc.*, 1892, **61**, 539).

1-*Dimethylaminobenzthiazole hydrodibromide*.—A solution of the dimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was gradually treated with bromine (0·6 c.c.) and the solution was heated on a water-bath under reflux for 5 minutes, transferred to a crystallising basin and concentrated under reduced pressure at laboratory temperature. On rubbing with a glass rod, the hydrodibromide formed small red crystals which were collected on porous earthenware and dried in a vacuum, m.p. 91-93° (decomp., after previous softening). [Found: Br (total), 48·1; Br (labile), 23·8. $C_9H_{10}N_2S$, HBr(Br) requires Br (total), 47·3; Br (labile), 23·7 per cent]. On reduction with sulphurous acid and basification with ammonia, the hydrodibromide yielded 1-dimethylaminobenzthiazole which separated from benzene-petroleum in glistening flakes, m.p. 87°. (Found: S, 17·7. Calc. S, 18·0 per cent).

5-*Bromo*-1-*dimethylaminobenzthiazole hydrotetrabromide*.—A solution of *s*-phenyldimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 3 c.c. of chloroform), and the mixture was heated under reflux for 20 minutes and concentrated under reduced pressure at laboratory temperature. The hydrotetrabromide crystallised in orange red prisms which had m. p. 100° (decomp.) after drying in a vacuum. [Found: Br. (total). 69·0; Br (labile), 41·3. $C_9H_9N_2BrS$, HBr (Br_3) requires Br (total), 69·1; Br (labile), 41·5 per cent). On reduction with sulphurous acid and basification with ammonia, the hydrotetrabromide yielded 5-*bromo*-1-*dimethylaminobenzthiazole*, which crystallised from petroleum-benzene in stout prisms, m.p. 167°. (Found: Br, 30·9. $C_9H_9N_2BrS$ requires Br, 31·1 per cent).

Synthesis of 5-*Bromo*-1-*dimethylaminobenzthiazole from* p-*Bromophenylthiocarbimide by way of* s-p-*bromophenyldimethylthiocarbamide*. (*i*) s-p-*Bromophenyldimethylthiocarbamide*, prepared from *p*-bromophenylthiocarbimide (2 g.) in benzene (20 c.c.) and a 33 % solution of dimethylamine in alcohol (1·2 c.c.), crystallised from benzene in small needles, m.p. 159°. (Found: Br, 30·8. $C_9H_{11}N_2BrS$ requires Br, 30·9 per cent). (*ii*) A solution of this thiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (1 c.c. in 3 c.c. of chloroform), and the mixture was heated under reflux for 25 minutes. The product

obtained by removing the solvent in a vacuum at laboratory temperature was reduced with sulphurous acid, basified and recrystallised from petroleum-benzene when 5-bromo-1-dimethylaminobenzthiazole was obtained in stout prisms which had m.p. 167° alone; and when mixed with the specimen obtained by bromination of *s*-phenyldimethylthiocarbamide.

1-*Dimethylamino-5-methylbenzthiazole hydrodibromide*.—A solution of *s*-*p*-tolyldimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (0·5 c.c. dissolved in 2 c.c. of the same solvent) and the solution was heated under reflux for 5 minutes and thereafter concentrated under reduced pressure at laboratory temperature. The *hydrodibromide* of the 5-methylbenzthiazole formed small orange prisms, m.p. 90° after drying. [Found: Br (total), 44·8; Br (labile), 22·2. $C_{10}H_{12}N_2S$, HBr (Br) requires Br (total), 45·3; Br (labile), 22·6 per cent). On reduction with sulphurous acid, this bromo-addition compound yielded 1-dimethylaminobenzthiazole, which separated from alcohol in small prisms, m.p. 86° (Hunter and Styles, *loc. cit.*).

3-*Bromo*-1-*dimethylamino*-5-*methylbenzthiazole hydrotetrabromide*.—A solution of *s*-*p*-tolyldimethylthiocarbamide (2 g.) in chloroform (15 c.c.) was treated with bromine (2 c.c.) and the mixture was heated under reflux for 20 minutes and thereafter concentrated in a vacuum at laboratory temperature. The *hydrotetrabromide* crystallised in glistening orange red needles, m.p. 95° (decomp.). [Found: Br (total), 67·2; Br (labile). 40·3. $C_{10}H_{11}N_2BrS$, $HBr(Br_3)$ requires Br (total), 67·6; Br (labile), 40·6 per cent]. On reduction with sulphurous acid the hydrotetrabromide yielded 3-*bromo*-1-*dimethylamino*-5-*methylbenzthiazole*, which crystallised from alcohol in needles, m.p. 169°. (Found: Br, 29·8. $C_{10}H_{11}N_2BrS$ requires Br, 29·5 per cent).

Synthesis of 3-*bromo*-1-*dimethylamino*-5-*methylbenzthiazole from* s-o-*bromo*-p-*tolyldimethylthiocarbamide*. s-o-*Bromo*-p-*tolyldimethylthiocarbamide*, prepared from *o*-bromo-*p*-tolylthiocarbimide (2 g.) and dimethylamine in benzene, crystallised in needles, m.p. 158°. (Found: Br, 29·5. $C_{10}H_{13}N_2BrS$ requires Br, 29·3 per cent). On cyclisation by treatment with bromine in the usual way and reduction of the product with sulphurous acid, 3-bromo-1-dimethylamino-5-methylbenzthiazole was obtained which had m.p. 169° alone, and when mixed with the specimen already described.

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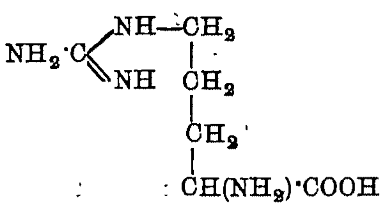
Synthesis of Purine Derivatives from Glyoxalines.

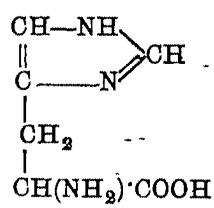
By P. C. Mitter and Nripendranath Chatterjee.

The synthesis of purine derivatives has been hitherto accomplished mainly *via* pyrimidines. The alternative process of synthesis *via* glyoxaline was first suggested by Windaus and Knoop (*Hofmeister's Beiträge zur chemischen Physiologie und Pathologie*, 1905, **6**, 392) in connection with the formation of methyliminazole by the action of ammonia (or zinc hydroxide-ammonia) on grape sugar and also other sugars. They write 'Gelingt es, die Methyl-gruppe (des Methylimidazols) zu oxidieren und eine Kondensation z.B. mit Harnstoff zu erzielen so erhielte man direct Xanthin. Andere Paarlinge wie Guanidin könnten in gleicher Weise zu Guanin, Hypoxanthin usw. führen."

Johnson (*J. Amer. Chem. Soc.*, 1914, **36**, 338) tried to prepare purines from glyoxalines or hydantoins but without success.

Speaking before the London Chemical Society on ' Newer standpoints in the Theory of Nutrition" Hopkins compared the structure of arginine and histidine with that of the purine base guanine (*J. Chem. Soc.*, 1916, **109**, 629); and pointed to some experiments which prove that the presence or absence respectively of *arginine and histidine* from





the food of an animal has a very considerable effect on purine metabolism as indicated by allantoin excretion, there being a very marked fall as the result of their withdrawal whilst their restoration is followed by a rise.*

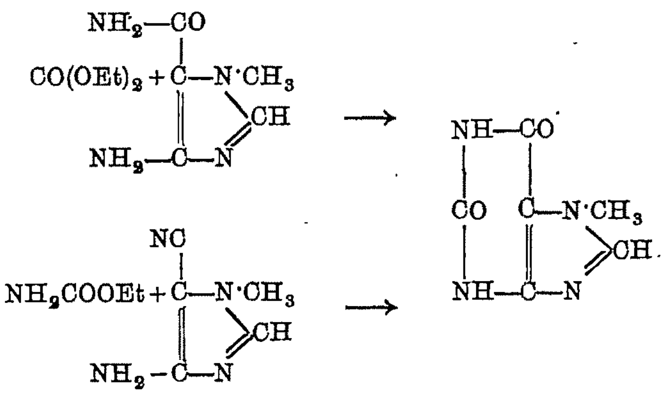
Fargher and Pyman (*J. Chem. Soc.*, 1919, **115**, 217) attempted to prepare 4-aminoglyoxaline-5-carboxylic acid with a view to obtain

* In a subsequent communication (*Biochem. J.*, 1916. **10**, 551) Ackroyd and Hopkins have demonstrated that the absence of one or the other is without any apparent effect on growth.

xanthine by condensing the substance with cyanic acid an subsequently eliminating water. They failed, however, to prepare the amino-acid.

With the same object in view, King and Murch (*J. Chem. Soc.*, 1923, **123**, 621) prepared ethyl 4-bromoglyoxaline-5-carboxylate, but the small yield precluded systematic attempts to condense the ester with carbamide.

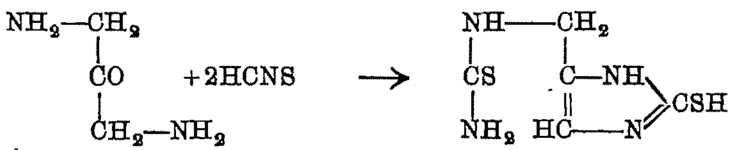
A purine derivative, heteroxanthine, was first prepared by Sarasin and Wegmann (*Helv. Chim. Acta*, 1924, **7**, 713) by heating the amide of 4-amino-1-methylglyoxaline-5-carboxylic acid with ethyl carbonate at 160-70°. Plaza (*Anal. Fis. Quim*, 1926, **24**, 731) employed the same reaction for the preparation of 8-methyl-7-ethylxanthine from 4-amino-2-methyl-1-ethylglyoxaline-5-carboxylamide. Montequi (*Anal. Fis. Quim.*, 1927, **25**, 182) obtained 8-methyl-7-ethylxanthine and also heteroxanthine by heating 5-cyano-4-amino-2-methyl-1-ethylglyoxaline and 5-cyano-4-amino-1-methylglyoxaline respectively with urethane.



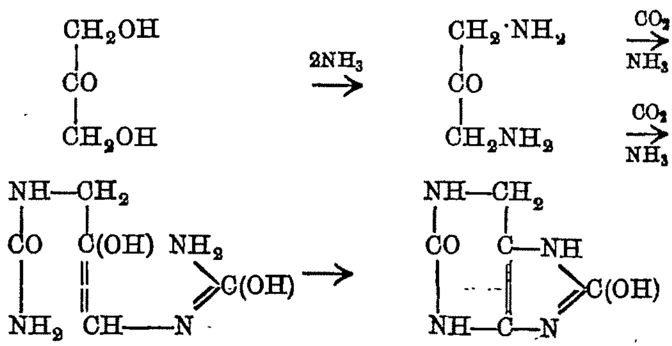
On an analysis of the mechanism of these reactions we find that in both the cases, eight out of the nine members constituting the purine skeleton are present in the starting material chosen while the ninth member, consisting of a carbon atom, is introduced subsequently between two N atoms. Not only do the reactions take place at high temperatures but it is difficult to imagine a simple reaction likely to take place in nature, giving rise to a substance containing the requisite carbon-nitrogen framework.

The difficulty is obviated when we recall the observations of Pyman (*J. Chem. Soc.*, 1911, **99**, 669) that diaminoacetone dihydrochloride gives by the action of potassium thiocyanate 2-thiol-4 (or 5)-amino-

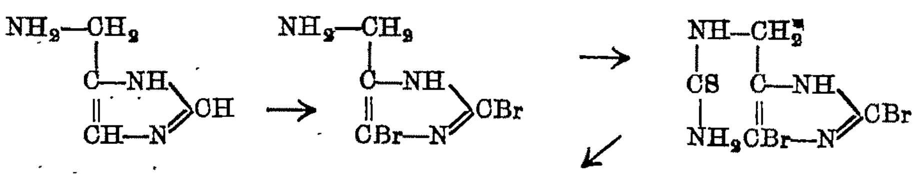
methylglyoxaline and 2-thiol-4 (or 5)-thiocarbamidomethylglyoxaline.



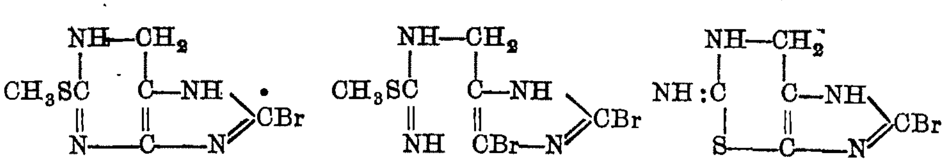
It will be observed that the substance contains the purine skeleton and a similar reaction between diaminoacetone and cyanic acid is quite likely to lead to the formation of purine derivatives in nature.



We have been strengthened in our supposition as we have been able to realise the scheme outlined above, though in a somewhat modified form.



(I) (II) (III)



(VI) (V) (IV)

When 4 (or 5)-aminomethylglyoxaline hydrochloride (Pyman, *loc. cit.*) is brominated in hydrobromic acid solution, 2:4-dibromo-5-aminomethylglyoxaline (II) is obtained in solution, while a tribromo compound, apparently the bromoamine, is precipitated. The filtrate on basifying gives (II) which on treatment with potassium thiocyanate gives (III) which readily undergoes ring-closure with the formation of a substance (IV) containing a fused thiazoline-glyoxaline ring.

If, however, the product is first methylated and then digested in alcoholic solution with pyridine, ring formation takes place in the desired manner with the formation of a purine derivative (2-methylmercapto-8-bromo-1.6-dihydropurine).

Experimental.

2:4-*Dibromo-5-aminomethylglyoxaline.*—5(or 4)-Aminomethylglyoxaline hydrochloride (1 g.), prepared according to the method of Pyman (*J. Chem. Soc.*, 1911, **99**, 668, 2172), was dissolved in water (20 c.c.) and 3 c.c. of 36% hydrobromic acid added. To the solution, bromine was added (0·6 c.c.) drop by drop, when a light yellow crystalline product (0·14 g.) separated. It is a tribromo compound, m.p. 214°. (Found: N, 12·9. $C_4H_4N_3Br_3$ requires N, 12·5 per cent).

The tribromo compound was filtered and the filtrate evaporated to dryness on the water-bath, dissolved in water and neutralised with dilute potassium carbonate solution. The precipitate after recrystallisation from water melts with decomposition at 280°. (Found: C, 18·4; H, 2·0; N, 16·1; Br, 62·2. $C_4H_5N_3Br_2$ requires C, 18·8; H, 1·9; N, 16·4; Br, 62·7 per cent).

2:4-*Dibromo-5-thiocarbamidomethylglyoxaline*.—Potassium thiocyanate (0·16 g.) was dissolved in a small quantity of hot water and the calculated amount of 2:4-dibromo-5-aminomethylglyoxaline gradually added. The mixture was heated on the water-bath for about 2 hours, cooled and filtered. After repeated crystallisation from water a crystalline mass was obtained, m.p. 252° (decomp.). (Found: C, 18·8; H, 1·9; N, 17·6. $C_5H_6N_4Br_2S$ requires C, 19·1; H, 1·9; N, 17·8 per cent).

2:4-*Dibromo-5-methylthiocarbamidomethylglyoxaline.*—Methylation was effected by moistening the finely powdered mercaptan with alcohol and then adding the calculated quantity of methyl iodide to it. It was shaken well and allowed to stand overnight. It was then

filtered and crystallised from dilute alcohol, m.p. 220° (decomp.). (Found: N, 16·6. $C_6H_8N_4Br_2S$ requires N, 17·0 per cent).

2-*Methylmercapto*-8-*bromo*-1:6-*dihydropurine*.—The methylated product was taken up in absolute alcohol and heated on the water-bath under reflux with the addition of a small quantity of pyridine for 5 hours. The alcohol was evaporated and the process repeated. The product was repeatedly crystallised from alcohol, m.p. 198-200°. (Found: N, 22·4. $C_6H_7N_4BrS$ requires N, 22·6 per cent). It gives the murexide reaction.

Thiazolinoglyoxaline derivative was obtained by refluxing 2:4-dibromo-5-thiocarbamidomethylglyoxaline in alcohol with a small quantity of pyridine. Nodules from dilute alcohol, m.p. 165°. (Found: N, 23·8. $C_5H_5N_4BrS$ requires N, 24·0 per cent).

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o-Aldehydocarboxylic Acids. Part II. A Synthesis of 4-Methoxyphthalaldehydic Acid and a New Synthesis of Opianic Acid.

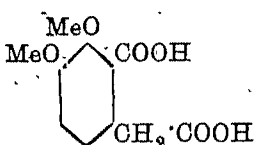
BY SATYENDRA NATH CHAKRAVARTI AND MAHADEVAN SWAMINATHAN.

4-Methoxyphthalaldehydic acid, for the synthesis of which several unsuccessful attempts have been made in the past, has now been synthesised by methods similar to those employed in the case of ψ-opianic acid and *m*-opianic acid (Chakravarti and Swaminathan, *J. Indian Chem. Soc.*, 1934, **11**, 715).

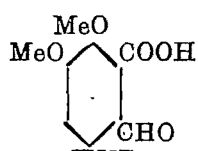
5-Methoxyhomophthalic acid (I)* was oxidised in boiling xylene solution by means of selenium dioxide to 4-methoxyphthalonic acid (II) which was isol[illegible] aniline salt (III). The aniline salt was then tran[illegible]ilino-4-methoxyphthalaldehydic acid (IV) by [illegible] which in its turn was hydrolysed to 4-[illegible]. p. 141.°

4-Methoxyphthalaldehydic acid gives on reduction 5-methoxyphthalide (VI), m.p. 119°, in an excellent yield It also forms an oxime.

In a similar manner, opianic acid (VIII), which has so far been obtained only as a degradation product of a number of alkaloids, and from meconine (Perkin and Stoyle, *J. Chem. Soc.*, 1923, **123**, 3172; Edwards, Perkin and Stoyle, *ibid.*, 1925, **127**, 195), has now been synthesised from 3:4-dimethoxyhomophthalic acid (VII) * in a good yield.



(VII)



(VIII)

EXPERIMENTAL

4-Methoxyphthalaldehydic acid (V). ... ophthalic acid (5 g.) was suspended in dry xylene (5 ... heated ... The boiling mixture ...

On hydrolysing the Schiff's base with dilute hydrochloric acid, 4-methoxyphthalaldehydic acid was obtained as needles, which after repeated crystallisation from water melted at 141°. (Found: C, 59·8; H, 4·7. $C_9H_8O_4$ requires C, 60·0; H, 4·4 per cent). The acid is readily soluble in the usual solvents. A mixed melting point with 5-methoxyphthalaldehydic acid, m. p. 144°, obtained by one of us by the oxidation of 2:6-dimethoxynaphthalene (Chakravarti, *J. Indian Chem. Soc.*, 1933, **10**, 696) showed considerable depression.

5-Methoxyphthalide (VI).—4-Methoxyphthalaldehydic acid (0·2 g.) was dissolved in dilute sodium hydroxide solution (5%, 5 c.c.) and reduced carefully with excess of sodium amalgam (6 g. of 4 %). The aqueous solution was made strongly acid and heated on the steam bath for 15 minutes, when the phthalide separated in almost theoretical yield. On recrystallisation from water it was obtained as prismatic needles, m.p. 119°. (Found: C, 65·7; H, 4·9. $C_9H_8O_3$ requires C, 65·8; H, 4·9 per cent).

Opianic acid.—3:4-Dimethoxyhomophthalic acid was prepared according to the method of Haworth, Koepfli and Perkin (*J. Chem. Soc.*, 1927, 551). This acid, which had been obtained as an oil by the above authors, has now been obtained in a crystalline form. It crystallises from benzene in colourless prisms, m. p. 116°. (Found: C, 54·8; H, 5·2. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0 per cent).

3:4-Dimethoxyhomphthalic acid (1 g.) was then oxidised to the corresponding phthalonic acid and the latter converted into the aniline derivative under conditions similar to those described in the previous case. The aniline derivative (0·6 g.) crystallised from alcohol in shining needles, m. p. 156°.

The aniline salt (0·5 g.) was suspended in dry xylene (5 c.c.) and the mixture boiled for 1½ hours in a reflux apparatus, when a clear solution was obtained. On cooling a mass of crystals separated which after repeated crystallisations melted at 187-88° and was found to be identical with the aniline derivative of opianic acid.

On hydrolysing the Schiff's base with dilute hydrochloric acid, opianic acid was obtained, which after repeated crystallisation melted at 150°. A mixed melting point with an authentic specimen caused no depression. (Found: C, 57·0; H, 5·1. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8 per cent).

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Studies in the Xanthone Group.

By Anukul Chandra Sircar and Sobhan Chandra Dutt.

γ-Pyrone ring is known to possess fairly developed chromogenetic properties. Though some of the hydroxyxanthones (*viz.*, gentisin and euxanthone) have been used for dyeing purposes, they are all feeble dyestuffs of yellow shades only. No attempt appears to have been made to introduce groups, specially those having chromophoric nuclei, in xanthone molecule and thereby obtain derivatives which would in all probability possess more interesting and well developed tinctorial properties and. therefore, better adapted for dying purpose. Dhar (*J. Chem. Soc.*, 1916, **109**, 749) described the preparation of a few(three only) azo derivatives from nitroamino xanthone, but their tinctorial properties were not studied.

The present investigation was undertaken mainly with the object of preparing such derivatives of xanthone as are expected to be useful for dyeing purpose.

Of the various possible simple monoamino derivatives of xanthone 3-aminoxanthone, being the only one which is definitely known, was mostly utilised as the starting material.

A number of azo compounds have been prepared by coupling diazotised 3-aminoxanthone with various phenols and amines such as, phenol, resorcinol, salicylic acid, β-naphthol, 2-hydroxy-3-naphthoic acid, G-acid, R-acid and dimethylaniline. Most of these azo derivatives resist all attempts to crystallisation (*cf.* Dhar, *loc. cit.*). They dye wool from 1% sulphuric acid bath and silk from acetic acid bath in shades varying from yellow to light pink.

It was expected that the acylaminoxanthones, *e.g.*, 3-benzoylaminoxanthone, 2-nitro-7-benzoylaminoxanthone and oxaldi-3-xanthonylamide would give vat dyes like the acylaminoanthraquinones (*cf.* D. Z. 16772; F. P. 400653, etc.) and acylaminophenanthraqninones (*cf.* Mukherjee and Watson, *J. Chem. Soc.*, 1916, **109**, 619) but the benzoylaminoxanthones were found to be almost colourless and the oxal derivative, though coloured, could not be made to yield a soluble vat.

The azomethine group, like the azo-linking, is known to enhance tinctorial properties (*cf.* Green and Sen, *J. Chem. Soc.*, 1910, **97**, 2242; Morgan and Reeves, *ibid*, 1922, **121**, 1; Sircar and Sen-Gupta, *J. Indian Chem. Soc.*, 1924, **1**, 321).

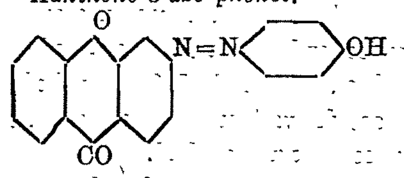
An azomethine group was introduced into the xanthone molecule by the condensation of 3-aminoxanthone with various aromatic aldehydes (*vide* experimental) and it has been found that the xanthone

phenylazomethines, though coloured, are not at all suitable for dyeing purposes. They are very unstable easily hydrolysing even by boiling water.

Two new derivatives of xanthone, namely 3-iodoxanthone and 2-nitro-7-iodoxanthone have been prepared from the corresponding amino compounds *via* diazo reaction.

Experimental.

Xanthone-3-azo-phenol.



A solution of 3-aminoxanthone (1 mol.) in hydrochloric acid (2½ mols.) was cooled to 0° and diazotised in the usual way with sodium nitrite (1 mol.). When the diazotisation was complete the mixture was treated with one molecule of phenol dissolved in excess of caustic soda. After two hours the reaction product was separated as a red precipitate by acidification. It crystallised from pyridine as deep orange-red small rhombic plates, not melting below 300°. It dissolves in acetic acid or sulphuric acid with a red colour. It is not satisfactorily absorbed either by wool or silk. (Found: N, 9·3. $C_{19}H_{12}O_3N_2$ requires N, 8·8 per cent). The other azo compounds prepared are described in Table I.

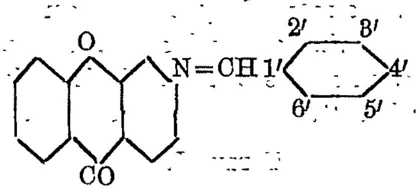
3-*Benzoylaminoxanthone* was prepared from 3-aminoxanthone and benzoyl chloride in presence of pyridine. The precipitate obtained on the addition of sufficient ether to the well cooled solution crystallised from alcohol as white shining plates, m. p. 212°. It is soluble in alcohol or acetone, benzene or chloroform. (Found: N, 4·8. $C_{20}H_{13}O_3N$ requires N, 4·45 per cent).

2-*Nitro-7-benzoylaminoxanthone*, prepared from 2-nitro-7-amino-xanthone, crystallised from pyridine in light yellow plates not melting below 300°. It is soluble in nitrobenzene or pyridine but insoluble in alcohol or acetone. It gives a very light yellow colouration with concentrated sulphuric acid. (Found: N, 8·1. $C_{20}H_{12}O_5N_2$ requires N, 7·7 per cent).

Oxaldi-3-xanthonylamide.—To a solution of 3-aminoxanthone (2 mols.) in pyridine oxalyl chloride (1 mol.) was added and the mixture shaken vigorously, when the red colour of the solution gradually changed to light brown. The mixture was heated on a water-bath

for ½ hour. The resulting product was precipitated by the addition of ether and obtained as a light reddish brown powder. It is only sparingly soluble in alcohol but readily so in pyridine from which it was purified by precipitation with ether. It does not melt below 300°. It could not be reduced to a soluble vat. It gives a light brown colouration with concentrated sulphuric acid. (Found: N, 6·1. $C_{28}H_{16}O_6N_2$ requires N, 5·8 per cent).

Xanthone-3(1′-azomethine benzene).



To a solution of 3-aminoxanthone (1 mol.) in the minimum quantity of hot alcohol benzaldehyde (1 mol.) was added and the mixture heated gently on a water-bath for about an hour when yellow needles began to separate. The heating was continued for one hour more, when reaction was complete. The solid mass was then collected and washed several times with dilute alcohol, after which it was crystallised from pyridine in fine yellow needles melting at 158°. It is practically insoluble in alcohol or benzene but soluble in nitrobenzene or pyridine. It gives a light yellow colouration with concentrated sulphuric acid. (Found: N, 4·62. $C_{20}H_{13}O_2N$ requires N, 4·68 per cent). The other azomethine compounds are described in Table II.

3-Iodoxanthone.—A well-cooled solution of 3-aminoxanthone (1 g.) in hydrochloric (3 c.c. in 25 c.c. water) was treated with sodium nitrite (0·3 g. in 3 c.c. water). An excess of well-cooled potassium iodide solution was then run into the diazo solution and the mixture left at the room temperature for about 6 hours after which it was heated on the water-bath till the evolution of nitrogen ceased completely. The solution was then triturated with excess of sodium thiosulphate solution, filtered and the iodo compound crystallised from pyridine in beautiful plates having a very light brown (almost white) colour. It melts at 173°. It is soluble in pyridine or nitrobenzene but insoluble in alcohol, acetone and sparingly soluble in carbon disulphide. (Found: I, 40·0. $C_{13}H_7O_2I$ requires I, 39·4 per cent).

2-*Iodo*-7-*nitroxanthone.*—2-Amino-7-nitroxanthone (3 g.) was dissolved in concentrated hydrochloric acid (8 c.c.) to which 75 c.c. of water had been added. The whole solution was cooled to 5° and the amino group diazotised by the slow addition of sodium nitrite (0·7 g.

dissolved in 5 c.c. of water cooled to 0°) with constant stirring. After the completion of diazotisation excess of potassium iodide solution was added and the mixture well-stirred. After the addition was complete the mixture was allowed to remain at the room temperature for about two hours after which it was gently heated on the water-bath till the evolution of nitrogen had ceased. The solid mass consisting of a mixture of the iodo compound and free iodine was then triturated with sodium thiosulphate solution in order to remove the excess of iodine. The resulting nitro-iodo-compound crystallised from pyridine in beautiful prismatic plates having a light brown colour, m.p. 285°. It is soluble in pyridine or nitrobenzene but insoluble in alcohol, acetone or benzene. (Found: I, 35·1. $C_{13}H_6O_4NI$ requires I, 34·65 per cent).

TABLE I.

Name of the compound and formula.	Method of preparation. Diazotised 3-amino xanthone +	Does not melt below	Analysis (N). Found.	Calc.	Remarks.
Xanthone-3-1'-azo-2'-naphthol ($C_{23}H_{14}O_3N_2$)	β-Naphthol	300°	8·1	7·6	Deep red microcrystalline powder from acetic acid, soluble in H_2SO_4 (pink). Dyes silk and wool light orange shades from acetic acid and sulphuric acid bath respectively.
Xanthone-3-1'-azo-4'-hydroxy-3'-benzoic acid ($C_{20}H_{12}O_5N_2$).	Salicylic acid	300°	8·4	7·8	Brown powder from acetic acid gives brown colour with conc. H_2SO_4.
Xanthone-3-1'-azo-2'-hydroxy-3'-naphthoic acid ($C_{24}H_{14}O_5N_2$).	2-Hydroxy-3-naphthoic acid	300°	6·81	6·8	Deep red powder from acetic acid, gives a reddish violet colouration with H_2SO_4 Dyes silk and wool in very light pink shades.
Xanthone-3-1'-azo-2'-naphthol-6' : 8'-disulphonic acid ($C_{23}H_{14}O_9N_2S_2$).	G-acid	...	5·65	5·3	Deep scarlet-red powder from acetone, soluble in H_2SO_4 (reddish violet). Dyes silk a golden yellow shade.
Xanthone-3-1'-azo-2'-naphthol-3' : 6'-disulphonic acid ($C_{23}H_{14}O_9N_2S_2$).	R-acid	...	5·6	5·3	Dark reddish-brown powder from acetone, soluble in H_2SO_4 (pink). Dyes silk and wool a reddish-orange shade.
Xanthone-3-1'-azo-2 : 4'-dihydroxybenzene ($C_{19}H_{12}O_4N_2$).	Resorcinol	...	8·9	8·4	Dark brown powder from acetic acid, soluble in H_2SO_4 (reddish-brown). Dyes yellow shades on wool and silk.
Xanthone-3-1'-azo-4' dimethylaminobenzene ($C_{21}H_{17}O_2N_3$).	Dimethyl aniline	...	12·5	12·2	Brownish-pink microcrystalline powder from acetone, soluble in H_2SO_4 (pink). Dyes silk and wool a pink shade.

TABLE II.

Name of the compound and formula.	Method of preparation. 8-Amino-xanthone +	M.p.	Analysis (N). Found	Calc.	Remarks.
Xanthone-8 (1′-azomethine-2′-hydroxybenzene). ($C_{20}H_{13}O_3N$).	Salicylaldehyde	256°	4·8	4·4	Needles from a mixture of nitrobenzene and alcohol.
Xanthone-8 (1′-azomethine-4′-hydroxybenzene). ($C_{20}H_{13}O_3N$).	p-Hydroxybenzaldehyde	264°	4·5	4·4	Prismatic plates from dilute alcohol.
Xanthone-8 (1′-azomethine-3′-hydroxybenzene). ($C_{20}H_{13}O_3N$).	m-Hydroxybenzaldehyde	275°	4·7	4·4	Yellow plates from alcohol.
Xanthone-8 (1′-azomethine-2′: 4′-dihydroxybenzene). ($C_{20}H_{13}O_4N$).	β-Resorcylic aldehyde	does not melt below 290°	4.7	4·2	Deep reddish-brown shining cubes (mixed with prisms) from dilute pyridine.
Xanthone-8 (1′-azomethine-3′-methoxy-4′-hydroxybenzene). ($C_{21}H_{15}O_4N$).	Vanillin	241°	4·37	4·06	Deep yellow microcrystalline powder.
Xanthone-8 (1′-azomethine-4′-dimethyl aminobenzene). ($C_{22}H_{18}O_2N_2$).	p-Dimethyl-amino-benzaldehyde	does not melt below 300°	7·9	8·2	Deep yellow powder.
Xanthone 8 (1′-azomethine-4′-chlorobenzene) ($C_{20}H_{12}O_2NCl$).	p-Chlorobenzaldehyde	,,	Cl, 10·6	11·3	Yellow microcrystalline powder.
Xanthone-8 (1′-azomethine-4′-acetylaminobenzene). ($C_{22}H_{16}O_3N_2$).	p-Acetyl-amino-benzaldehyde	,,	N, 8·0	8·4	Light yellow powder.
Xanthone-8-cinnamylidene-1′-azomethine ($C_{22}H_{15}O_2N$).	Cinnamic aldehyde	,,	N, 4·7	4·2	Deep brown plates from pyridine.

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The Constancy of the Ratio of Carbon to Nitrogen in Natural Systems Undergoing Oxidation and the Problem of Protein Synthesis.

By N. R. Dhar.

In publications (Dhar, "New Conceptions in Biochemistry"; 1932; *J. Indian Chem. Soc.*, 1933, **10**, 699; 1934, **11**, 145) from these laboratories, it has been emphasised that the phenomenon of oxidation is only of importance to animal life but is of great importance to plant and soil processes and the laws governing all these oxidations appear to be identical.

The phenomenon of oxidation taking place in nature has been found to be markedly accelerated by sunlight, increase of temperature of the reacting systems and the presence of inductors (iron compound) and surfaces acting as catalytic agents.

In tropical countries, where there is plenty of sunshine, the influence of light and increased temperature due to the absorption of solar energy, play important rôle in animal, plant and soil oxidation reactions.

In this communication it will be shown that the constancy of C:N ratio exists not only in the soil but is also observed in animal metabolism as well. It seems that when a mixture of organic compounds containing nitrogenous substances present in natural systems undergoes oxidation in air, a constant ratio of C:N is finally attained.

Constancy of C:N *ratio in the Products of Oxidation in Soil and in the Animal Body.*

Analysis of different soils with various amounts of organic matter shows a nearly constant ratio between the elements carbon and nitrogen. This ratio which has the value 10 varies within narrow limits in normal soils. It is well known that in soil, which is well ærated, the chemical changes affecting carbon and nitrogen present in the soil are intimately connected. The combined nitrogen existing in soil can form nitrate only if the ratio of C to N is smaller than 10. When the proportion of carbon is greater, the excess is oxidised to CO_2 and the nitrogen remains as protein. When on the other-hand, the proportion of nitrogen becomes greater than the above ratio, the nitrogenous compound is converted into ammonia and nitrate, which may be absorbed by the plant or lost from the soil through different agencies. The observations of Leighty and Shorey

(*Soil Science*, 1930, **30**, 257) that in the majority of soils examined by them, C:N ratio varied from 7 to 15 and in extreme cases the ratio could be as small as 3 and as large as 35. It seems to the author that the soils examined by these workers were not properly aërated for a sufficiently long time. The following results obtained by Lyon, Bizzell and Wilson (*J. Amer. Chem. Agron.*, 1923, **15**, 457) show that no available nitrogen is added to the soil when a large amount of cellulose or other carbonaceous compound is present with the nitrogenous material added as fertilisers.

TABLE I.

Nitrate content of soil to which roots were added and left to decompose for 3 months.

Material used.	Nitrogen.	Wt. of roots added.	Nitrate nitrogen in leachings.
Control soil	...	...	946·6 mg.
Oat roots	0·45%	133·3 g.	207·3
Timothy roots	0·62	96·8	398·4
Maize roots	0·79	75·9	510·6
Clover roots	1·71	35·1	924·4
Dried blood	10·71	5·6	1751·1

It will be evident from the following experiments of Sievers and Holtz (*Washington State Coll. Agric. Expt. Sta. Bull.*, 1926, **43**, 206) that not only the ratio of carbon to nitrogen existing in soil is constant but the ratio of carbon to nitrogen oxidised from the organic substances present in soil is also nearly constant and has the value not far from 10.

TABLE II.

Decomposition of soil organic matter for 142 days.

Nitrogen in soil	Carbon in soil.	C : N ratio in soil.	CO_2 liberated (as carbon).	Nitrate nitrogen formed, parts per million.	C : N ratio of the oxidation products.
0·091%	0·910%	10·0	119·6 mg.	15·4	7·8
0·143	1·684	11·8	187·6	18·3	10·2
0·155	1·860	12·0	167·5	17·6	9·5
0·233	2·889	12·4	230·9	26·3	8·8

The constancy of C:N in the soil processes has been ascribed to the activities of micro organisms but it will be evident from the following considerations that the constancy of C:N may be maintained even in the absence of bacteria in many natural systems undergoing oxidation.

It has been observed that in the presence of sodium arsenite, which does not oxidise when exposed to air but becomes oxidised to sodium arsenate when added to sodium sulphite, which is readily oxidised in air, the velocity of the oxidation of sodium sulphite by air is markedly retarded. Similarly, the presence of carbohydrates, which are themselves oxidised when mixed with sodium sulphite, ferrous hydroxide or cerous hydroxide or any other suitable reducing agent, markedly diminishes the velocity of the oxidation of the last named substances. We have arrived at the generalisation that in oxidation reactions, the phenomenon of negative catalysis is observed when the catalyst is a reducing agent.

Moreover, carbohydrates, fats and proteins have been oxidised by simply passing air through solutions or suspensions of these substances in presence of sunlight. Palit and Dhar (*J. Phys. Chem.*, 1928, **32**, 1263; 1930, **34**, 711, 993) have carried out experiments on the induced and photochemical oxidations of mixtures of carbohydrates, fats and proteins with each other and have arrived at the interesting conclusion that the presence of any one of these substances, which is itself undergoing oxidation, retards the oxidation of others.

In normal health, the heat and energy of the body are supplied to the system from the simultaneous combustion of carbohydrates, fats and proteins. The results obtained in these laboratories conclusively prove that the oxidation of fat is retarded by carbohydrates and perhaps less powerfully by proteins. Physiologists have reported that if all the carbohydrates in the food is replaced by fat, the fat is incompletely oxidised. In other words, for the complete combustion of fat in the body, carbohydrate must burn. V. Plimmer and R. H. A. Plimmer ("Vitamins and the Choice of Food," 1922, p. 5) have stated the position in the following words:—"Mixed with carbohydrate, it is as if fats burn with a clear flame but if there is too little carbohydrate, it burns smokily. The half burnt products of fat are poisonous to the body and produce coma." Similar results have been obtained by Chakravarti and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 617) *in vitro* and it has been observed that the velocity

of the oxidation of fats and fatty acids is decreased by the presence of carbohydrates and the amount of acetone bodies obtained by the oxidation of fats and fatty acids by H_2O_2 and iron salts decrease considerably when carbohydrates are added to the fats. Hence for the complete oxidation of fats, their velocity of oxidation must be decreased by carbohydrates *in vitro* and *in vivo*. It seems fairly certain now that the presence of either one or two of the above substances, which are undergoing oxidation, retards the oxidation of the third. It is, therefore, evident that in the presence of a large excess of carbohydrate or fat, little protein is burnt. The protein-sparing qualities of carbohydrates and fats were discovered from feeding experiments by some of the earliest students of metabolism and it is believed that carbohydrates are the more efficient of the two in sparing proteins. It has also been proved by Lusk, Landegren and others (compare Lusk, "Science of Nutrition", 1919, p. 269) that the withdrawal of carbohydrates from the food increases the protein metabolism. Moreover, in diabetes, where the glucose passes out unoxidised, there is considerable waste of tissue protein.

It will be interesting to note that in starvation, the ratio of carbon to nitrogen metabolism (oxidation) is not far from 10 to 1 as will be evident from the following table.

TABLE III.

Animal	Dog	Fowl	Guineapig	Rabbit
Ratio of C and N oxidised in starvation	9·5	10·8	7·6	9·7

The above results have been calculated from the observations recorded in Lusk's "Science of Nutrition", 1919, p. 86.

If the starvation is continued further, the value of C:N becomes less than 10, as will be seen in the following results obtained with a dog kept on long starvation.

TABLE IV.

Days of starvation	4th-13th	14th-15th	16th-23rd	24th-30th	31st-35th	36th	37th	38th
Ratio of C and N oxidation starvation	10·3	9·3	9·01	8·6	8·0	6·0	5·8	5·5

These results have been calculated from the observations of Voit (*Z. Biol.*, 1901, **41**, 545). In other words, in long-continued starvation leading to death, the ratio of carbon to nitrogen undergoing oxidation, nearly attains the value 6, which is nearly the ratio

of carbon to nitrogen present in the animal body. It appears that in animal metabolism, the oxidation of carbonaceous substances (fats and carbohydrates) and proteins is guided by more or less the same relations as obtained in the soil and both these oxidation processes appear to be similar in nature.

In the soil, tho oxidation of carbonaceous matter and proteins seems to be similarly controlled. The carbonaceous substances, such as cellulose, lignin, pentosan, glucose, etc., added to the soil retard the oxidation of the amino acids obtained from protein decomposition and hence in presence of large amounts of straw, hay, etc., very little amino acid oxidation to ammonia by air is possible and thus the nitrogen in the protein, present in the soil, remains unavoidable for the plants. Just as the process of ammonification in soil is retarded by carbonaceous matter, similarly the process of nitrification is also slowed down by carbonaceous matter, because both ammonification and nitrification are mainly oxidation reactions.

In the following tables obtained from the results of Lipman and associates [*N.J. Agr. Exp. Sta. Bull.*, 1912, 247] the retarding influence of carbohydrates on ammonification is well brought out.

TABLE V.

Organic substance 4 g.	Total nitrogen in substance.	Ammonia formed in milligrams. No carbohydrate.	Glucose 2 g.	Sucrose 2 g.	Starch 2 g.
Wheat flour	94·8	5·14	3·66	5·84	1·56
Cowpea meal	156·8	50·88	31·71	28·57	23·70
Linseed meal	247·0	110·69	96·01	60·78	68·34
Soybean meal	245·6	129·64	108·03	94·88	54·36
Cotton seed meal	246·1	123·63	99·67	97·23	54·54
Corn meal	51·2	1·18	1·30	1 04	0·69

TABLE VI.

Influence of sugar on ammonia formation from 2% peptone solution.

Incubation period.	Sugar added.	NH_3-N in 100 c.c.
5 days	0%	44·80 mg.
5	1	40·74
5	2	14·14
5	5	1·26
5	20	0
15	0	73·08
15	1	50·68
15	2	36·54
15	5	33·04
15	20	0

Similarly the addition of glucose to casein causes a decrease in the amount of casein decomposed and ammonia formed. The same behaviour is also observed with glucose and dried blood.

The results of Hill (*Virginia Agric. Exp. Station Tech. Bull.*, 1915, 6) recorded in the following table show that the addition of carbonaceous matter to soil leads to the decrease in nitrate formation.

TABLE VII.

Nitric nitrogen in milligrams in 100 grams dry soil.

		After, weeks					
Organic matter added (0·8-0·6 per cent.).	At the beginning.	12	20	24	28	32	40
None	0·59	0·74	0·55	1·25	1·50	3·51	2·65
Paper	0·59	0	0	trace	trace	0·20	1·20

The addition of one per cent dextrose to soil markedly retards the formation of nitrate in soil.

It is generally believed that the nitrite and nitrate forming bacteria can live mainly on the energy obtained from the oxidations of ammonium salt to nitrite and nitrite to nitrate and glucose, peptone, gelatine, asparagine and other organic substances are harmful. This follows from the view point advanced in this paper. The organic substances act as retarding agents in the oxidation of ammonium salts to nitrite and of nitrite to nitrate and hence the energy supply to the bacteria is cut off and their growth checked by the presence of organic sub stances, which act as negative catalysts in the oxidation processes.

From the foregoing considerations, it is clear that the carbonaceous matter present in soil acts as an agent in sparing the soil protein from oxidation, just as carbohydrates preserve the body protein from undergoing oxidation. The retarding influence of carbohydrates and other carbonaceous compounds on the rate of oxidation of proteins to ammonia and of ammonium salts to nitrite has been observed with different types of micro-organisms having different protein and energy requirements. Moreover, this retarding influence is not restricted to oxidations due to micro-organisms. Investigations carried on in the author's laboratories show that this phenomenon of the decrease of the velocity of oxidation is of general occurrence and is observed with catalytic, induced and photochemical oxidation reactions involving a mixture of organic compounds containing nitrogenous substances. (Compare Dhar, "New Conceptions in Biochemistry," 1932, p. 44; Palit

and Dhar, *J. Phys. Chem.*, 1930, **34**, 711). The current explanation of the retarding influence of carbonaceous compounds on protein oxidation and the constancy of C : N ratio in soils, based on the energy requirements of the micro-organisms first emphasised by Doryland (*N. Dakota Agric. Expt. Sta. Bull.*, 1916. 116) has to be revised in view of the fact that the retarding effect appears to be a general phenomenon occurring in chemical, catalytic, physiological, soil and photochemical oxidation processes in which a mixture of organic compounds is underg tion. Moreover, there is considerable loss of energy in the process of deaminisation of proteins and hence the energy requirements of the micro-organisms may not be the controlling factor in regulating the amounts of proteins and carbohydrates oxidised in soil processes.

Ratio of C : N *and Protein Synthesis.*

Recently the authors (Dhar and Mukherji, *J. Indian Chem. Soc.*, 1934, **11**, 727) have shown that amino acids are readily formed *in vitro* by the reaction of solutions of nitrates and carbohydrates or substances which produce carbohydrates when exposed to sunlight in presence of titania and no amino acid is synthesised in the dark or by the reaction of ammonium salts and carbohydrates even in light. Moreover, we have been able to produce evidence showing the formation of arginine *in vitro* by exposing solutions of glucose and potassium nitrate to sunlight in presence of titania. It is well known that the percentage of arginine is largest amongst the amino acids obtained from plant proteins. It seems, therefore, that the amino acids in plants are synthesised from carbohydrates and nitrates and that sunlight is an important agency in this reaction and the plant pigments are likely to behave as photo-sensitisers, just as titania acts as a sensitiser in the photosynthesis of amino acids *in vitro*.

Moreover, it will be evident from Table II that the nitrate concentration of the soil decreases when carbonaceous matters like oat roots, timothy rooots, maize roots etc., are added. Apart from the formation of proteins by the action of the micro-organisms on the nitrates and carbonaceous substances, it is possible that amino acids are also photosynthesised by the reaction of nitrates and carbonaceous compounds in presence of light. This photosynthesis of amino acids may be responsible for the decrease of nitrate concentration in soil when carbonaceous compounds are added.

It has been stated that the rice plant takes up ammonium salts in the beginning of its development and nitrate in the end. Moreover plants like barley, maize, and pumpkins, which are rich in carbohydrates, readily absorb ammonium salts. It seems that in these plants, in the beginning, the plants contain a very large amount of carbohydrate and little protein and thus the C:N ratio may be much greater than 10:1 and hence the ammonia is absorbed; whilst in the end the protein accumulation takes place due to the energy supplied by the oxidation of carbohydrates and thus the ratio of C:N has a tendency to have the value 10:1 and that is why ammonium salts are not required. Hence it seems that where the C:N ratio is much greater than 10:1, ammonium salts may be absorbed. However, the legumes and beans should at no stage grow with ammonium salts. On the other hand, starch producing plants at certain stages when the carbohydrate content is high and protein content low, may be fed and made to grow well by ammonium salts. It is believed that the ease of ammonia absorption depends on the velocity with which it is converted into asparagine and this in turn depends on the amount of carbohydrates, which are also necessary for protein synthesis.

Conclusion.

The following conclusions have been arrived at from a comprehensive estimate of the results of the author and other workers.

1. Not only the ratio of carbon to nitrogen in the compound existing in soil is constant but the ratio of carbon to nitrogen in the products of oxidation of organic compounds in soil is also nearly constant and is approximately 10.

2. In starvation, the ratio of carbon to nitrogen oxidised in the metabolism of different animals is also not far from 10. It seems that when a mixture of organic compounds undergoes oxidation in air the ratio of carbon to nitrogen oxidised is nearly 10 and this appears to be a general phenomenon.

3. Just as carbohydrates preserve the body protein from undergoing oxidation, the carbonaceous matter present in the soil protects the soil protein from oxidation. The retarding influence of carbohydrates and other carbonaceous compounds on the oxidation of proteins to ammonia and ammonium salts to nitrite has been observed with different micro-organism having varied protein and

energy requirements and hence it is assumed that the energy requirements of the micro-organisms may not be the controlling factor in regulating the amounts of proteins and carbohydrates oxidised in soil processes.

4. The protein-sparing qualities of carbohydrates arise from the fact that carbohydrates decrease the oxidation of proteins when both these groups of substances undergo oxidation and this behaviour forms a part of the generalisation that the phenomenon of negative catalysis (retardation) is observed in an oxidation reaction, when the catalyst is a reducing agent.

5. Amino acids are readily synthesised *in vitro* when a solution of a nitrate and carbohydrates is exposed to sunlight in presence of titania It seems likely that the energy obtained from the oxidation of carbohydrates by nitrates or oxygen is necessary for protein synthesis in plants. The assimilation of ammonium salts by plants in protein synthesis is possible when the carbohydrate content is high and depends on the C : N ratio.

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Studies in the Anthraquinone Series.

By P. C. Mitter, Satindrajiban Das-Gupta and Sumatichand Bachhwat.

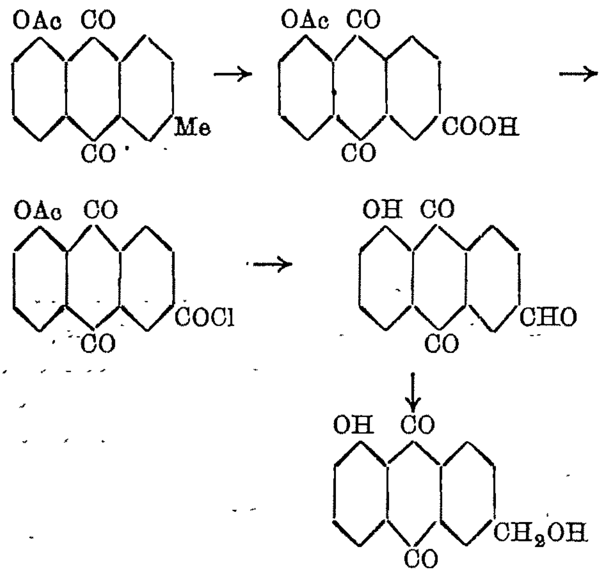
Among the hydroxy-anthraquinones occurring in nature, there is only one which is known to contain a carbinol group, namely Aloe-emodin (1:8-dihydroxy-anthraquinone-3-carbinol). On account of the well-known physiological properties of this substance, it appeared to us to be of interest to prepare and study the properties of other hydroxy-anthraquinone-carbinols of the same type but containing a smaller number of hydroxyl groups. In this connection, we have prepared 1-hydroxyanthraquinone-6-carboxylic acid and 1-hydroxyanthraquinone-6 carbinol and also 1-hydroxyanthraquinone-3-carboxylic acid and 1-hydroxyanthraquinone-3-carbinol.

The therapeutic properties of the substances have not yet been studied

1-Hydroxy-6-methyl-anthraquinone (Mitter and Sarkar, *J. Indian Chem. Soc.*, 1930, **7**, 619), was acetylated and the acetyl derivative was oxidised by chromic acid in a solution of glacial acetic acid and acetic anhydride (Fischer, Falco and Gross; *J. pr. Chem.*, 1911, *ii*, **83**, 208) whereby 1-hydroxyanthraquinone-6-carboxylic acid was obtained after deacetylation. The acid was re-acetylated and then converted into the acid chloride by treatment with thionyl chloride. The acid chloride was reduced to the aldehyde by passing a slow stream of pure and dry hydrogen through a solution of the substance in pure xylene at 130-40° in presence of palladiumised barium sulphate and on hydrolysis 1-hydroxy-6-aldehydo-anthraquinone was obtained. (Rosenmund, *Ber.*, 1918, **51**, 585; Rosenmund and Zetzche, *Ber.*, 1921, **54**, 425, Mitter and Banerjee, *J. Indian Chem. Soc.*, 1932, **9**, 375).

The aldehyde was next reduced catalytically by means of hydrogen in presence of platinum oxide with ferrous chloride as promoter when 1-hydroxyanthraquinone-6-carbinol was obtained. (Roger Adams and co-workers, *J. Amer. Chem. Soc.*, 1922, **44**, 1937; 1923, **45**, 2171;

1924, 46, 1675; Mitter and Banerjee, *loc. cit.*)



1-Hydroxy-8-methyl anthraquinone was prepared according to the method of Bentley, Gardner and Weizmann (*J. Chem. Soc.*, 1907, **91**, 1626), and acetylated with acetic anhydride in presence of a drop of strong sulphuric acid. The product was then oxidised with chromic acid (Fischer, Falco and Gross, *loc. cit.*). During subsequent operations the acetyl group was partially knocked off and it was found necessary to de-acetylate it completely with alcoholic potash and to reacetylate with acetic anhydride in presence of a drop of sulphuric acid. The conversion of the acetylated acid into the corresponding chloride and its subsequent reduction into aldehyde and alcohol followed exactly the lines of 1-acetoxy-anthraquinone-6-carboxylic acid.

Experimental.

(With Satindrajiban Das-Gupta).

1-*Acetoxy-6-methyl-anthraquinone.* — 1-Hydroxy-6-methyl-anthraquinone prepared according to the method of Mitter and Sarkar (*J. Indian Chem. Soc.*, 1930, **7**, 619) was treated with acetic anhydride and a few drops of strong sulphuric acid, the mixture warmed until a clear solution was obtained and allowed to stand for some time when

the acetyl derivative separated. The mixture was then poured into water, filtered and the residue crystallised from alcohol, m.p. 172°. The compound was previously obtained by Mitter and Sarkar (*loc. cit.*) but no experimental details were given.

1-*Hydroxy anthraquinone-6-carboxylic acid.*—1-Acetoxy-6-methyl-anthraquinone (2 g.) was dissolved in a mixture of acetic anhydride (35 c.c.) and glacial acetic acid (35 c.c.) and the solution heated on a water-bath at 60°. A chromic acid mixture was prepared by dissolving 4 g. of the acid in the least possible quantity of water and diluting with a mixture of 20 c.c. of glacial acetic acid and 20 c.c. of acetic anhydride. The oxidising mixture was added, 5 c.c. at a time, in rapid succession, to the above solution with occasional shaking. The mixture was kept at 60° for one hour and then heated at 100° on the water bath for another hour. Acetic acid and acetic anhydride were completely removed by distilling the mixture under reduced pressure and the residue boiled with moderately concentrated hydrochloric acid for about half an hour and then diluted with water and allowed to cool. The filtered and washed residue was slightly warmed with 5 % sodium carbonate solution, the extract acidified with hydrochloric acid and the precipitate filtered, washed and dried. Bright yellow needles from pyridine, m.p. 297°, yield nearly theoretical. (Found: C, 67·32; H, 3·37. $C_{15}H_8O_5$ requires C, 67·16; H, 2·98 per cent).

1-*Acetoxy-anthraquinone-6-carboxylic acid chloride.*—The acid was acetylated as in the case of the anthraquinone. Light yellow needles from glacial acetic acid, m.p. 242°. (Found: C, 66·16; H, 2·85. $C_{17}H_{10}O_6$ requires C, 65·80; H, 3·19 per cent). The acetylated product was refluxed with 25 to 30 times its weight of thionyl chloride on a water-bath for 2-3 hours when a clear solution was obtained and no hydrochloric acid could be detected at the mouth of the guard tube fitted at the mouth of the condenser. Thionyl chloride was completely removed by distilling under reduced pressure and the residue crystallised from benzene as yellow crystals, m.p. 182°. (Found: Cl, 11·51. $C_{17}H_9O_5Cl$ requires Cl, 10·80 per cent).

1-*Hydroxy-6-aldehydo-anthraquinone.*—0·4 G. of the acetylated acid chloride and 0·2 g. of the palladiumised barium sulphate (Rosenmund, *loc. cit.*) was introduced into a flask containing 25 c.c. of very pure and dry xylene and provided with a side tube and an upright condenser. Hydrogen gas generated in a Kipp's apparatus from pure zinc and sulphuric acid was purified and dried by passing successively

through $AgNO_3$ solution, $KMnO_4$ solution, KOH solution, concentrated sulphuric acid, and finally phosphorus pentoxide and passed through the mixture at the rate of one to two bubbles per second while the flask was maintained at 130-40°. The open end of the condenser was fitted with a calcium chloride guard tube.

The reaction was completed in about 2 hours when hydrochloric acid gas could scarcely be detected at the end of the guard tube. The contents of the flask were then filtered, the filtrate shaken with 50 c.c. of 10% sodium bisulphite solution in a mechanical shaker and the aqueous layer separated and boiled with concentrated hydrochloric acid for about half an hour when the aldehyde was precipitated. Brown needles from glacial acetic acid, m.p. 194°, yield 0 15 g. (Found: C, 71·02; H, 2·81. $C_{15}H_8O_4$ requires C, 71·42; H, 3·17 per cent).

1-*Hydroxyanthraquinone*-6-*carbinol*.—0·1 G. of platinum oxide catalyst (Roger Adams and others, *loc. cit.*) 0·2 g. of the aldehyde, sodium ethoxide equivalent to 0·36 c.c. of a millimolar solution and ferrous chloride equivalent to 0·5 c.c. of a 0·2 molar solution were introduced in the order given into a clean and dry hydrogenating flask, 150 c.c. of absolute alcohol introduced and the flask evacuated by means of a water pump until the alcohol began to boil. The flask was then connected with the hydrogenation apparatus and the gas introduced while the flask was mechanically shaken until there was no further absorption of hydrogen. The absorption was complete in about 10 minutes. The contents of the flask were filtered and the filtrate distilled under diminished pressure to remove the alcohol and the residue crystallised first from 50% acetic acid and then from toluene when orange needles were obtained, m.p. 160-62°. (Found: C, 70·98; H, 3·88. $C_{15}H_{10}O_4$ requires C, 70·86; H, 3·93 per cent).

(WITH SUMATICHAND BACHHWAT).

1-*Acetoxy*-3-*methyl-anthraquinone*.—Sharp pale yellow needles from acetic acid, m.p. 156°. (Found: C, 72·6; H, 4·3. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3 per cent).

1-*Hydroxyanthraquinone*-3-*carboxylic acid*.—Yellow woolly needles from pyridine or glacial acetic acid, m.p. 282-84°. (Found: C, 66·9; H, 3·5. $C_{15}H_8O_5$ requires C, 67·1; H, 3·0 per cent).

1-*Acetoxy-anthraquinone*-3-*carboxylic acid*.—Greenish yellow silky needles from acetic acid, m.p. 276°. (Found: C, 65·9; H, 3·2. $C_{17}H_{10}O_6$ requires C, 65·8; H, 3·2 per cent).

1-*Acetoxy-anthraquinone-3-carboxylic acid chloride*.—Pale yellow micro-crystals from benzene, m.p. 162-63°. (Found: Cl, 10·2. $C_{17}H_9O_5Cl$ requires Cl, 10·8 per cent).

1-*Hydroxyanthraquinone-3-aldehyde*.—The temperature was maintained at 140-45° for 3-4 hours and then at 148° for another 2 hours while the current of hydrogen was increased. At the end of about 6 hours from the beginning of the operation, no hydrochloric acid could be detected at the mouth of the guard tube. Dark brown needles from glacial acetic acid, m.p. 214° (with sublimation). (Found: C, 72·0; H, 3·20. $C_{15}H_8O_4$ requires C, 71·4; H, 3·17 per cent).

1-*Hydroxyanthraquinone-3-carbinol*.—0·2 G. of 1-hydroxy-anthraquinone-3-aldehyde was introduced into the reduction flask with 0·1 g. of platinum oxide, 0·36 millimole of sodium ethoxide and 0·1 millimole of ferrous chloride and absolute alcohol, just sufficient to dissolve the aldehyde. The reduction was complete in 5-10 minutes. The mass left after the removal of alcohol was first crystallised from dilute acetic acid. On further crystallisation from toluene, orange needles were obtained, m.p. 197-99°. (Found: C, 70·7; H, 3·96. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·93 per cent).

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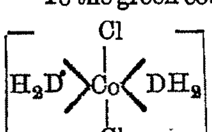
Compounds of Dimethylglyoxime with Cobaltous Chloride.

By Dines Chandra Sen and Priyadaranjan Rây.

Feigl and Rubinstein (*Annalen*, 1923, **433**, 183) have described the preparation of a dark olive-green compound in acetone solution from crystalline cobaltous chloride and dimethylglyoxime. As the substance does not respond to any usual tests for Co^{++}, such as by sulphuretted hydrogen, caustic potash, rubeanic acid, etc., nor for the dimethylglyoxime, such as by the addition of nickel salts, they assume that the compound is a strong cobaltous complex of formula $[DH_2{\cdot}Co{\cdot}DH_2]Cl_2$ where $DH_2 = \begin{array}{l} CH_3{\cdot}C{=}NOH \\ \quad\; | \\ CH_3{\cdot}C{=}NOH \end{array}$, with a co-ordination number four for cobalt. Thilo and Heilborn (*Ber.*, 1931, **64**, 1441), starting from anhydrous cobaltous chloride and dimethylglyoxime in acetone solution, have prepared a deep red crystalline substance having the same composition as that of the green compound described by Feigl. The red compound is very unstable and passes readily in solution (in acetone), specially in the presence of a trace of water, into the stable green modification. The chlorine atoms in both the compounds are precipitated by silver nitrate.

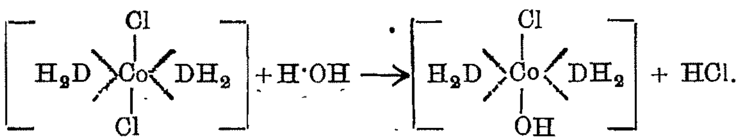
The constitution of these compounds have been discussed by Thilo and his co-workers (Thilo and Friedrich, *Ber.*,1929, **62**, 2990; Thilo and Heilborn, *loc. cit.*). According to them, it is the red compound which should be represented by the above constitution $[DH_2{\cdot}Co{\cdot}DH_2]Cl_2$.

To the green compound they attribute the constitution for the following reason.



The central cobalt atom is here hexa-co-ordinated with non-ionic chlorine atoms. Feigl and Rubinstein (*loc. cit.*) have already mentioned that the green compound hydrolyses in aqueous solution which, therefore, reacts acid, the compound dissolving with a brown colour. Thilo and Heilborn (*loc. cit.*) assume that this is not a case of ordinary hydrolysis, but the substitution

of chlorine atom in the complex by the OH group of water leading to the formation of hydroxy compounds and HCl, which then reacts with $AgNO_3$.



This is also supported by Feigl and Rubinstein's (*loc. cit.*) isolation of the compound $(DH_2)_2 \cdot Co \cdot (OH)Br$. Hieber and Leutert (*Ber.*, 1927, **60**, 2296,) have also shown that the green compound in acetone solution is a non-electrolyte. That the chlorine atoms are in the *trans*-position, is inferred by Thilo from the behaviour of the corresponding bromide towards ethylenediamine (*cf.* Feigl and Rubinstein, *loc. cit.*), as the Br atoms are not replaced by a single bidentate group like ethylenediamine.

With a view to throw more light upon the constitution of these interesting and much discussed compounds, a further study of their properties was undertaken, the results of which are embodied in the present paper.

It might be recalled here that instances of strong cobaltous complexes of the highly stable type, as represented by the above green salt, are extremely rare. Among the known strong cobaltous complexes, mention can be made only of potassium cobaltocyanide which is very unstable, and of cobalt biguanide and cobalt rubeanate, which are highly insoluble.

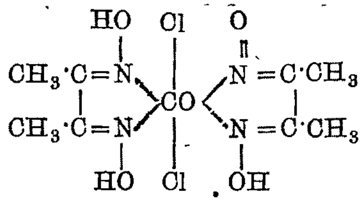
It is well known that the magnetic susceptibility of a paramagnetic ion usually undergoes a profound alteration, when the latter forms the central atom of a perfect complex. It has been further established that all complex cobaltic compounds are diamagnetic, though Co^{++} or Co^{+++} are strongly paramagnetic, having magnetic moments of about 24 and 14 Weiss's magnetons respectively. All cobaltous complexes so far examined, excepting the three just mentioned above, exhibit the same susceptibility value as the Co^{++} in the simple salts. Of the above mentioned three compounds, only potassium cobaltocyanide is diamagnetic, cobalt biguanide and cobalt rubeanate, each shows a susceptibility value of 10 Weiss's magnetons approximately. The case of these compounds has previously been discussed (Rây, *Proc. Indian Science Congress*, 1932, p. 141, *Presidential*

Address, Chem. Soc.; Rây and Bhar, *J. Indian Chem. Soc.*, 1928, 5, 497). Magnetic susceptibility is thus found to be a more or less unfailing guide in determining the complex character, as well as the valency, of the central paramagnetic ion. In the case of Feigl's green compound the susceptibility measurement showed that the compound is diamagnetic. This fact, taken together with the characteristic properties of the substance, such as its solubility, hydrolysis, etc., strongly suggests that in this compound the central cobalt atom is in the tervalent stage. In other words, the salt represents a cobaltic complex. It has also been possible to isolate the first product of its hydrolysis. This latter, which has the composition $[DH_2 \cdot Co \cdot DH(OH)Cl]$ and resembles the corresponding bromide already described by Feigl, is also diamagnetic, showing that the valency of the central Co atom remains unchanged during the hydrolysis. The green salt also slowly liberates iodine from KI solution, indicating a higher stage of valency for the cobalt atom. It has been further observed that when a solution of cobaltous salt is mixed with one of dimethylglyoxime in alcohol, the colour of the cobalt salt changes, and the mixture slowly liberates iodine from acidified KI solution.

The hydrolysis of the salt has been further studied in aqueous solution. It is an established fact of complex chemistry that unstable weak acidic or basic ions are stabilised or strengthened by complex formation. When $CoCl_2$ does not appreciably hydrolyse, there is no reason why it should do so to such a marked extent after combination with dimethylglyoxime. For, it has been found that the hydrolysis in aqueous solution is complete. Hence the Cl atoms, as has already been pointed out by Thilo, Hieber and Leutert (*loc. cit.*) are inside the complex zone ; the central Co atom must, therefore, be in a higher state of oxidation.

From the considerations set forth above, it can be concluded that Feigl's green salt is not a tetra-co-ordinated cobaltous complex as suggested by him, nor is it a hexa-co-ordinated cobaltous complex as assumed by Thilo and his co-workers. This naturally applies to all the other so-called cobaltous complexes, related to this green salt, described by Feigl and Rubinstein (*loc., cit.*) and also to the compound described by Dübsky and Brychta (*Chem. Zentr.*, 1929, II, 549).

The constitution of the green compound should, therefore, be represented by the formula in which one of the hydrogen atoms of one dimethylglyoxime molecule is replaced by the cobalt atom :



The green colour of the salt, as well as its reaction with ethylenediamine (Thilo, *loc. cit.*), indicates that it is a *trans*-dichloro compound.

The oxidation of cobaltous atom into cobaltic stage occurs evidently in a spontaneous way during its reaction with dimethylglyoxime. Such instances of spontaneous oxidation during complex formation are not rare in the case of Co atom (*cf.* Rây, *Z. anorg. Chem.*, 1932, **208**, 393; Rây and Chackrabarty, *ibid.*, 1933, **211**, 176).

On the other hand, Thilo's red isomer gives a susceptibility value of 19·04 Weiss's magnetons, a value which a Co^{++} should theoretically possess according to Bose-Stoner's view. Ordinary simple cobaltous salts, solid or in solution (*e. g.* $CoSO_4$, $CoCl_2$, etc.), give, however, a susceptibility value of 24—25 Weiss's magnetons. In a fourfold co-ordination compound this value has been found to be reduced somewhat—the lowest value found is 20·9 for $[Co(N_2H_4)_2]SO_3{\cdot}H_2O$ (Rây and Bhar, *J. Indian Chem. Soc.*, 1928, **5**, 499). Similar behaviour has also been observed in the case of nickel compounds as well. This discrepancy from the theoretical value has been attributed by Bose and Stoner to imperfect neutralisation of the orbital moments of the electrons by the field of neighbouring molecules and ions. In the present case of Thilo's red isomer, the orbital moments of the outer electrons of the Co atom appear, therefore, to be completely neutralised. The green and the red isomers are, therefore, sharply distinguished by their magnetic properties. The valence condition of the central Co atom is thus proved to be different in the two complexes, Feigl's green compound having the central Co atom in the tervalent stage, whereas Thilo's red isomer contains a bivalent cobalt. The properties of red isomer also lead to the same conclusion as has already been pointed out by Thilo and Heilborn (*loc. cit.*).

We have also tried to prepare Dübsky and Brychta's black compound of the alleged composition and constitution $[DH_2{\cdot}Co{\cdot}DH]Cl$ (*loc. cit.*). Though a black crystalline compound, as described by them, has been obtained, its composition, however, does

not agree with the above formula. The analytical results correspond approximately to the formula [$2\,CoCl_2 \cdot 3DH_2 \cdot 3H_2O$]. The substance was found to be feebly magnetic. This suggests that it is an impure mixture of the green compound and its products of hydrolysis. The properties of the black crystals also resemble those of the green compound.

It is now clear that the green compound and its red isomer should be represented by the following constitutional formulæ.

$$\left[H_2D \searrow \overset{\text{Cl}}{\overset{|\ \text{III}}{\underset{\underset{\text{Cl}}{|}}{\text{Co}}}} \swarrow HD \right] \qquad [H_2D : \overset{\text{II}}{\text{Co}} : DH_2]Cl_2$$

Hexa-co-ordinated tervalent cobalt. Diamagnetic.

Tetra-co-ordinated bivalent cobalt. Strongly paramagnetic.

Experimental.

Feigl's Green Salt.

The compound was prepared, as described by Feigl and Rubinstein (*loc. cit.*), from $CoCl_2,6H_2O$ and dimethylglyoxime in acetone solution. (Found: Cl, 19·62; Co, 16·35. Calc., Cl, 19·60; Co, 16·30 per cent). The aqueous solution of the substance is strongly acid, liberates iodine slowly from acidified KI solution and evolves hydrogen with metallic zinc.

The magnetic susceptibility of the dry solid at $30° = \chi_m \times 10^6 = -0{\cdot}281$.

Molecular conductivity in aqueous solution at 18°.

v (dilution in litres)...	32	64	128	256	512	1024
M_V ...	335·7	354·1	362·2	374·6	...	388·7

The molecular conductivity of HCl at infinite dilution is about 381. This clearly indicates that the hydrolysis is complete in the sense of the equation:

$$H_2D{=}\underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Co}}}{=}HD + H_2O \longrightarrow H_2D{=}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Co}}}{=}HD + HCl,$$

and that the product of hydrolysis in presence of the liberated HCl is a non-electrolyte, the conductivity of the solution being equal to that of HCl only.

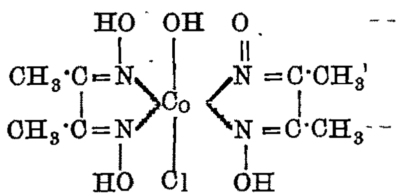
Chloro-hydroxo-dimethylglyoxime Cobalt.

When a saturated solution of the green salt was strongly cooled, a silky yellowish brown crystalline substance gradually separated.

This was washed with cold water and dried in vacuum over sulphuric acid. {Found: N,16·51; Cl,10·44; Co,17·16. $[DH_2 \cdot Co \cdot DH(OH)Cl$ requires N, 16·35; Cl, 10·37; Co, 17·18 per cent}. Magnetic susceptibility at 30° $= \chi_m \times 10^6 = -0 \cdot 053$.

The substance is sparingly soluble in water, giving a brown solution, which also reacts acid due to further hydrolysis.

The constitution of this brown compound should be represented, similarly to that of the green salt, as follows:



When the green compound was treated with aqueous ammonia, a yellow crystalline substance was obtained, containing both ammonia and chlorine. The aqueous solution of this compound also liberates iodine from acidified KI solution.

Thilo's Red Isomer.

This substance was prepared, as described by Thilo and Heilborn, from anhydrous $CoCl_2$ and dimethylglyoxime in dry acetone solution. The anhydrous cobalt chloride was prepared according to Baxter and Dorcas (*J. Amer. Chem. Soc.*, 1924, **46**, 362) by heating $CoCl_2$, $6H_2O$ in a current of dry HCl and N_2 to 300°. (Found: Cl, 20·11; Co, 16·42. Calc., Cl, 19·60; Co, 16·30 per cent). Magnetic susceptibility at 34° $= \chi_m \times 10^6 = 16 \cdot 58$, $\eta_{weiss} = 19 \cdot 04$ (corr.).

Dübsky's Black Compound.

The substance was prepared according to Dübsky and Brychta's method as abstracted in the Centralblatt (*loc. cit.*). (Found: N, 12·72; Cl, 20·16; Co, 17·64. $2COCl_2 \cdot 3DH_2 \cdot 3H_2O$ requires N, 12·69; Cl, 21·43; Co, 17·82, per cent).

It gave a susceptibility value of $\chi_m \times 10^6 = 0 \cdot 9557$ at 34°, $\eta_{weiss} = 4 \cdot 40$. The composition of the compound is not quite clear, and it appears to be contaminated with some decomposition product.

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A New Constant for Fixed Oils. Hypochlorous Acid Value.

By M. Goswami and K. L. Basu

In a preliminary note on the subject ((*Analyst*, 1934, 59, 538) the authors indicated the possibility of determining the unsaturation of fixed oils by means of hypochlorous acid,* which is a distinct improvement on the present methods of doing the same in many respects, especially in respect of time factor ; this being observed very carefully in other methods to avoid substitution. There were preliminary difficulties, *e.g.*, interference of alcohol, indicator, stability of sodium hypochlorite solution, etc., and after numerous experiments the following method has been standardised.

The oil or fat is saponified with alcoholic potash, the excess of KOH neutralised by HCl, alcohol driven off and the soap is diluted with water ; a dilute solution of sodium hypochlorite of known strength is then added and the whole acidified with calculated amount of dilute H_2SO_4 (to liberate the whole of hypochlorous acid) and kept for 5 to 15 minutes. After absorption the excess of HOCl is then determined by adding KI solution and titrating the liberated iodine. The calculated and theoretical values as deduced from Iodine values are found to agree very fairly even within the time factor of 2 hours. The additional advantages of this process are the following:—

(1) The saponification value is determined simultaneously without recourse to second weighing.

(2) Time required for complete saturation is only 5 to 15 minutes.

(3) Before determining the value one need not know whether the oil or fat is drying, semi-drying or non-drying as is required in ordinary methods.

* It was thought that the oils would absorb the acid like $CH_2=CH_2$ in the following way :—

$$CH_2=CH_2 + HOCl \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$$

and there would be no substitution and therefore no question of time factor.

EXPERIMENTAL.

NaOCl solution (5 c.c., prepared from bleaching powder solution and Na_2CO_3, containing slight excess of Na_2CO_3 and approximately of the strength 5 c.c. = 20 − 25 c.c. of $\frac{N}{10}$ $Na_2S_2O_3$) and excess of KI solution are taken in a conical flask and acidified with H_2SO_4 (dil.), the iodine liberated is titrated with thiosulphate and the experiment is repeated with standard H_2SO_4 solution, the volume of the latter required to liberate just the full amount of iodine from the solution is thus determined.*

0·120-0·125 G. of oil is saponified in the usual way with 25 c.c. of approx. $N/5$ alcoholic KOH. The excess of the alkali is exactly neutralised with standard HCl using bromothymol blue as indicator. The alcohol is then evaporated off on the water-bath until a pasty mass remains. The soap is dissolved in water, transferred to a 750 c.c. flask and the solution diluted to 600 c.c. To this 5 c.c. of NaOCl solution is added followed by H_2SO_4 of known strength just to neutralise the free Na_2CO_3 and to liberate HOCl from the hypochlorite. The flask is quickly closed by means of a rubber stopper fitted with a dropping funnel containing KI solution, well stirred and kept in a dark and cool place for 5-15 mins. The KI solution in the funnel is then blown in and the flask well shaken. The dropping funnel is then washed and taken out. The solution is now acidified with excess of H_2SO_4 solution and the iodine liberated is titrated against standard thiosulphate. Blank experiment is done side by side. The difference in the thiosulphate figures gives the amount of HOCl absorbed (1 c.c. of N-thiosulphate = 0·002625 g. of HOCl).

* From the reactions :

(a) $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$

(b) $2NaOCl + H_2SO_4 = Na_2SO_4 + 2HOCl$

(c) $2\ HOCl + 4KI = 2\ KOH + 2\ KCl + 2\ I_2$

(d) $2\ KOH + H_2SO_4 = K_2SO_4 + 2\ H_2O$

the amounts of H_2SO_4 required to neutralise respectively Na_2CO_3 of the hypochlorous solution, to liberate HOCl and to neutralise KOH of equation (c) are determined. For example in a particular experiment 5 c.c. of NaOCl = 22·6 c.c. of 0·9819N/10-thio. and 3·25 c.c. of 0·9813N-H_2SO_4 is required to liberate iodine completely. Now 22·6 c.c. of 0·9819 N/10-thio. corresponds to 0·8268 g. of NaOCl and to liberate HOCl from this amount of the hypochlorite 1·192 c.c. of H_2SO_4 of the above strength is required whilst the same volume is necessary for KOH. Thus (3·25-2·384) *i.e.* 0·866 c.c. of 0·9813 N-H_2SO_4 is required for the neutralisation of the excess of Na_2CO_3 present in the hypochlorite solution. These calculations are necessary for knowing the exact amount of H_2SO_4 required for Na_2CO_3 and for NaOCl,

TABLE I.

Blank experiments performed for standardising the method.

Water added = 600 c.c. Vol. of NaOCl soln. = 5 c.c.

Expt.	Time[1].	H_2SO_4 (0·9818N).	Indicator used.	Thiosulphate (0·9819N) required.
1	2 hrs.	2·05 c.c.[2]	Nil	22·15 c.c.
2	2 hrs.	3·25 [3]	Nil [4]	22·15
3	30 mins.	2·05 [2]	Phenolphthalein	19·95
4	2 hrs.	2·05 [2]	Bromothymol blue [5]	22·15
5	2 hrs.	3·25 [3]	,,	22·15

[1] Time after which titration is made. [2] Amount required just to neutralise Na_2CO_3 and to decompose NaOCl. [3] Whole amount to liberate I_2 completely. [4] 1 % sol.—2 drs. [5] 1 % sol.—2 drs.

From the above experiments it is clear that phenolphthalein cannot be used as indicator after saponification for neutralisation of the excess of KOH and that bromothymol blue can safely be used. Interference of alcohol has also been investigated.

TABLE II.

Water added = 600 c.c. Thiosulphate required (blank) = 22·15 c.c. NaOCl soln. = 5 c.c.

Expt.	Time.	H_2SO_4 (0·9318N).	Alcohol.	Thio (0·9819N).
6	2 hrs.	* 2·05 c.c.	25 c.c.	20·1 c.c.
7	,,	† 3·25	,,	20·70
8	,,	* 2·05	10	21·0
9	30 mins.	,,	10	21·25
10	2 hrs.	,,	5	21·4
11	30 mins.	,,	5	21·55
12	2 hrs.	† 3·25	10	21·6
13	30 mins.	,,	10	22·00
14	2 hrs.	† 3·25	5	21·65
15	30 mins.	,,	5	22·15

* Amount just to neutralise Na_2CO_3 and to liberate HOCl from NaOCl completely.

† Whole amount of acid to liberate the I_2 completely.

Experiments Nos. 6-15 in Table II show that as the amount of alcohol decreases the thiosulphate figures approach the blank ones. Again when the whole amount of the acid is added the difference between the titration figures is smaller than when the exact amount of the acid (required for Na_2CO_3 and NaOCl) is added. The following experiments were done with pure sodium oleate using bromothymol blue as indicator showing that the soap absorbs HOCl.

TABLE III.

Water added=600 c.c. Vol. of NaOCl soln.=5 c.c. Na-oleate soln. =20 c.c.

Expt.	Time.	H_2SO_4 (0·9313*N*).	Thio. (0·9819*N*).	Blank thio without oleate.	Alcohol used.
16	2 hrs.	*2·05	12·80 c.c.	22·15 c.c.	Nil
17	,,	†3·25	12·45	...	...
18	,,	*2·05	12·3	21·00	10 c.c.
19	,,	†3·25	12·15	21·60	,,
20	,,	*2·05	12·15	20·1	25
21	,,	*3·25	12·15	20·70	..

* Amount just to neutralise Na_2CO_3 and to liberate HOCl from NaOCl completely.
† Amount to liberate I_2 completely.

Experiments Nos. 16-21 in Table III show that the whole amount of acid cannot be added when there is no alcohol. To get the best result the alcohol should be evaporated off after saponification.

In the following experiments with oils, the alcohol, after saponification value is determined, is evaporated off on the water-bath (the soap remaining as a pasty mass) and the acid (0·9313 N-H_2SO_4) is added just to neutralise the free Na_2CO_3 of the hypochlorite solution and to decompose NaOCl to HOCl. Iodine values by Wiji's method are determined simultaneously. These and the corresponding HOCl values (% of HOCl absorbed) as calculated from the latter are given for comparison in the tables.

Non-drying Oils.

TABLE IV.

Ground-nut oil.

I_2 value=87·6. NaOCl soln. =5 c.c. (=22·6 c.c. of thio. used). Corresponding HOCl value (called henceforward H. C. value)=18·09.

Wt. of oil.	Time.	Thio (0·9819*N*)	Blank thio.	Diff. thio.	HOCl absorbed.
0·1502 g.	15 mins.	11·50 c.c.	22·0 c.c.	10·50 c.c.	18·02 %
0·1598	1 hr.	11·20	22·05	10·85	17·5
0·1672	2 hrs.	10·50	22·0	11·50	17·78
*0·1584	5 mins.	12·05	22·0	9·95	16·72
*0·0864	5 ,,	16·15	22·05	5·9	17·6

* Shows that the absorption is not complete within 5 minutes with more than 0·15 g. of the oil.

Buffalo ghee (butter fat).

NaOCl soln. =7·5 c.c. (=26·15 c.c. of thio used).

Iodine value=35·4. Corresponding H. C. value=7·818.

Wt. of oil.	Time.	Thio *N*/10.	Blank thio.	Diff. thio.	HOCl absorbed.
0·1336 g.	2 hrs.	21·55 c.c.	25·50 c.c.	3·95 c.c.	7·76 %
0·1322	1 hr.	20·5	25·70	5·2	7·49
0·1414	15 mins	21·5	25·7	4·2	7·796

Cocoanut oil.

NaOCl soln. =7·5 c.c. (=26·0 c.c. of thio used).

Iodine value=9. Corresponding H. C. value=1·859.

Wt. of oil.	Time.	Thio (0·988*N*/10).	Blank thio.	Diff. thio.	HOCl absorbed.
0·1501 g.	2 hrs.	24·5 c.c.	25·6 c.c	1·1 c.c.	1·9 %
0·1560	1 hr.	24·45	25·75	1·3	2·16
0·1480	15 mins.	24·65	25·75	1·10	1·928

TABLE IV (continued).

NaOCl soln. =7·5 c.c. (=26·0 c.c. of thio. used).

Olive oil.

Iodine value=88 Corresponding H. C. value=18·18.

Wt. of oil.	Time.	Thio (0·988N/10).	Blank thio.	Diff. thio.	HOCl (absorbed)
0·1736 g.	2 hrs.	13·40	25·6	12·2	18·2
0·1627	1 hr.	14·55	25·7	11·15	17·77
0·1081	15 mins	18·35	25·7	7·35	17·64

Semi-drying Oils.

TABLE V.

Mustard oil.

Iodine value=108. Corresponding H. C. value=22·31.

0·1218 g.	2 hrs.	15·15	25·6	10·45	22·25 %
0·1073	1 hr.	16·15	25·6	9·45	22·84
0·1161	15 mins.	15·7	25·7	10·00	22·34

Sesame oil.

Iodine value=110. Corresponding H. C. value=22·73.

0·1281 g.	2 hrs.	14·5	25·6	11·1	22·43 %
0·1085	15 mins.	16·50	25·75	9·25	22·11
0·1235	1 hr.	14·95	25·7	10·75	22·57

Drying and Fish Oils.

TABLE VI.

Linseed oil.

Iodine value=185. Corresponding H. C. value=38·22.

0·1336 g.	2 hrs.	7·4 c.c.	25·6 c.c.	18·2 c.c.	35·33 %
0·0974	1 hr.	12·60	25·7	13·1	34·88
0·0861	15 mins.	14·05	25·7	11·65	35·10

Clupea ilisha oil.

Iodine value=88. Corresponding H. C. value=18·18.

0·1068 g.	2 hrs.	18·2	25·6	7·4	17·97
0·1005	1 hr.	18·8	25·7	6·9	17·80
0·0948	15 mins.	19·2	25·7	6·5	17·78

SUMMARY.

1. The method consists of the determination of percentage of absorption of HOCl by sodium salts of the fatty acids present in oils after saponification value is determined with bromothymol blue as indicator.

2. The technique of the process depends upon careful manipulation of the amount of sulphuric acid added just to liberate HOCl from NaOCl solution which is added to the soap solution and to neutralise free Na_2CO_3.

3. The alcohol used for the determination of saponification value need not be removed completely; soap thus obtained is then dissolved in water and treated with NaOCl.

4. Theoretical and calculated H. C. values agree very fairly.

5. Simultaneous determinations of saponification value and the degree of unsaturation are possible by the present method without recourse to second weighing.

6. Absorption is complete in 5 – 15 minutes with 0·15 g. of substance.

7. Time factor does not vitiate the result to any appreciable extent.

8. No preliminary sorting of oils as non-drying, semi-drying and drying is necessary as is required in other methods.

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Viscosity and Molecular Association.

By Balbhadra Prasad.

Attempts have been made from time to time to use viscosity data for elucidating the molecular association in the case of liquids. The most successful method used so far has been Bingham's fluidity method (Bingham and Harrison, *Z. physikal Chem.*, 1909, **66**, 1 ; Bingham, *J. Amer. Chem. Soc.*, 1910, **43**, 287; Turner, "Molecular Association," 1915, p. 78) in which Bingham compares the calculated and observed temperatures for a given fluidity (inverse of viscosity) usually 200 or 300 and finds out molecular association by dividing the observed temperature by the calculated temperature. He calculates the temperature at which the given fluidity is attained by assigning definite temperatures to every element and every kind of linkage for the given fluidity and assuming that the temperature at which the compound reaches the fluidity is the sum of the temperatures corresponding to the various atoms and linkages in the molecule. The method gives quite good results but there is no theory behind it. During the last few years much work has been done on the viscosity of liquids Now we know definitely that the viscosity changes with temperature in the case of unassociated liquids can be represented by the formula,

$$\log \eta = \alpha + \beta/T$$

where η denotes viscosity, T absolute temperature and α and β two constants (Raman, *Nature*, 1923, **111**, 532; Dunn, *Trans. Faraday Soc.*, 1926, **22**, 401; Andrade, *Nature*, 1930, **125**, 309: Sheppard, *Nature*, 1930, **125**, 489; Prasad, *J. Indian Chem. Soc.*, 1933, **10**, 143). This can be used for elucidating the molecular association of liquids as will be evident from what follows.

In the case of unassociated liquids since, $\log \eta = \left(\alpha + \frac{\beta}{T}\right) \Big/ \frac{\delta \log \eta}{\delta\left(\frac{1}{T}\right)}$.

which is equal to β, is constant whereas in the case of associated liquids it goes on decreasing with temperature, if the higher molecules break up into smaller ones. The author (*loc. cit.*) has shown that β generally increases with molecular weight. In the homologous series, β increases by about eighty for every increase in the molecule by C_2H_4 (*ibid.*) in the case of unassociated liquids. However it is not entirely a

function of molecular weight for the β values of normal and *iso*hydrocarbons differ by as much as 4% at times. When two or more simple molecules form an associated molecule the arrangement of the atoms in the molecule is not disturbed except when they combine irreversibly forming entirely different kinds of molecules, *e. g.*, the condensation of acetylene to benzene. The molecules in the case of associated liquids combine by weak co-valent linkages which are disrupted when the temperature is raised. When the difference between the β values of normal and *iso*hydrocarbons hardly exceeds 4%, we can safely assume that these weak co-valency linkages which exist between the molecules of a liquid forming associated molecules, will not alter the value of β except by increasing the average molecular weight. So it follows that

$$\frac{d\log\eta}{d\left(\frac{1}{T}\right)}\Bigg/_{T_1} \Bigg/ \frac{d\log\eta}{d\left(\frac{1}{T}\right)}\Bigg/_{T_2} = \frac{M_1}{M_2}$$ where M_1 and M_2 are the average molecular weights of the liquid at the temperatures T_1 and T_2. From the above it is evident that by knowing the value of $d\log\eta \Big/ d\left(\frac{1}{T}\right)$ for a number of temperatures in the case of any liquid, the molecular association for all other temperatures can be calculated in terms of the molecular weight at one definite temperature.

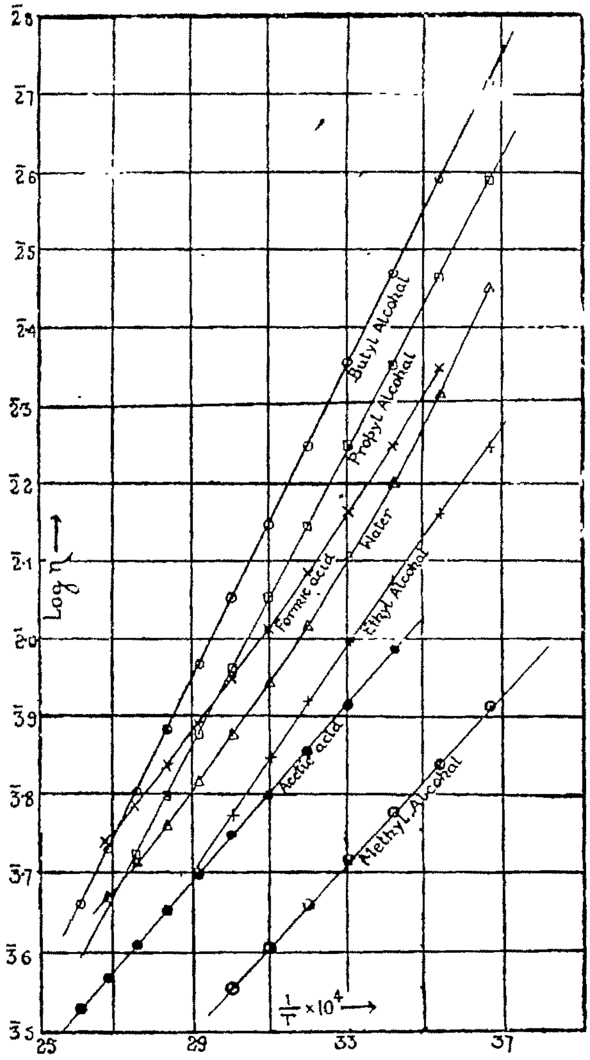
In Figure 1 log η is plotted against $1/T$ for water, methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, formic acid and acetic acid.

TABLE I.

Liquids.		5°.	25°	45°	65°	85°
Water	...	1041	870	763	680	686
Methyl alcohol	...	546	546	546	...	...
Ethyl alcohol	...	723	723	723	723	...
Propyl alcohol	...	946	946	946	946	946
Butyl alcohol	...	1009	1009	1009	1009	1009
Formic acid	...	...	774	725	655	655
Acetic acid	...	...	578	578	578	578

In Table I the values of $d\log\eta \Big/ d\left(\frac{1}{T}\right)$ calculated from the figure for above liquids at a number of temperatures are given.

Fig. 1.



To illustrate how the molecular association at any temperature can be calculated in terms of the molecular weight at another temperature, let us take the case of water. For water

$$\frac{\left.\dfrac{d\log\eta}{d\left(\dfrac{1}{T}\right)}\right/5^\circ}{\left.\dfrac{d\log\eta}{d\left(\dfrac{1}{T}\right)}\right/85^\circ}=\frac{1041}{636}$$

i.e., 1·6. So water at 5° is 1·6 times more associated on an average than at 85°. The constant value of β within any temperature range does not necessarily mean that the liquid is unassociated. All it means is that molecular association is not appreciably changing within this temperature range.

In order to find out the absolute value for molecular association, a method can be developed on the following lines.

The author has shown (*J. Indian Chem. Soc.*, 1933, **10**, 135) that $T_c/\text{B} = 0{\cdot}7$ (approx.) for an associated liquid when T_c denotes critical temperature on the absolute scale. If critical temperature is known we can approximately find out the value of β for any liquid. We can apply this to the associated liquids also and the values obtained will refer to the unassociated molecules, since much below the critical temperature even the associated liquids cease to be associated. From what has been said before $\dfrac{d \operatorname{Log} \eta}{d\left(\frac{1}{T}\right)} \Big/ \beta$ (determined from T_c) will be a measure of molecular association for the liquid at temperature T.

In Table II molecular association determined by this method is given. For the sake of comparison, the values determined by Eötvos-Ramsay method are also given.

TABLE II.

Liquids.		T_c.	β.	$t°$.	$\dfrac{d \log \eta}{d\left(\frac{1}{T}\right)}$.	x degree of molecular association.	x from Eötvos-Ramsay method.
Water	...	640	448	5°	1041	2·3	2·9
,,	...	...	...	25	870	1·9	2·3
,,	...	...	...	45	763	1·7	2·7
,,	...	...	...	65	680	1·5	2·6
Methyl alcohol	...	508	356	0 60	546	1·5	3·6
Ethyl alcohol	...	517	362	0·70	728	2·0	3·0
Propyl alcohol	...	547	383	0·90	946	2·5	2·1
Butyl alcohol	..	560	392	0·110	1009	2·5	...
Acetic acid	...	595	416	20 110	578	1·4	2·0

A glance at the values of molecular association determined by the two methods will show that the values do not always agree In the

case of water, surface tension method shows that the molecular association first increases and then decreases with temperature, whereas by this method we find a continuous decrease with temperature. In case of methyl alcohol, the value of molecular association from surface tension measurements is found to be 3·61, greater than that of water even — a fact which seems to be highly improbable considering that the boiling point of water is 35° greater than that of methyl alcohol in spite of the latter's higher molecular formula. By this method the molecular association is approximately 1·5 less than the molecular association of water. The most serious discrepancy is that the order of liquids arranged in descending order of molecular complexity is not found to be the same by the two methods. By the surface tension method we get a lower and lower value for molecular association in a homologous series as the molecular weight increases till we get absurd results sometimes. e.g., the molecular association in the case of stearic acid is found to be one half. By this method in the case of alcohols the molecular association seems to be increasing with the molecular weight, a fact which is very doubtful. This may partly be due to the approximate nature of the two assumptions (a) $\beta/T_c = 0\cdot7$ and

$$\frac{d \log \eta/d\left(\frac{1}{T}\right)}{T_1} \Bigg/ \frac{d \log \eta/d\left(\frac{1}{T}\right)}{T_2} = \frac{M_1}{M_2}.$$

We can get some idea of the error involved by the following considerations.

The author has shown (*J. Indian Chem. Soc.*, 1933, **10**, 135) that β/T_B (where T_B denotes the boiling point of liquids) varies from 1·04 to 1·24 in the case of nineteen liquids. From this we might expect that β/T_c would vary from 0·62 to 0·74. In the cases of eight liquids, β/T_c has been calculated in the same paper and is found to be within this limit. Further as $T_B/T_c = 0\cdot6$ is only approximately true, we might expect a little more variation in the values of β/T_c. β/T_c for such varied liquids as bromine, ethyl ether, ethyl propyl ether, chloroform, allyl chloride, methyl sulphide and heptane (not included in the above list) is also approximately equal to 0·7 From all this we can safely assume that it may fluctuate from 0·6 to 0·8 at the utmost in the case of unassociated liquids. Hence the maximum error involved in the calculation of β/T_c will be 14%. As the difference in the β values of normal and *iso*compounds, where the structural difference is greater than between the associated and unassociated liquids, is about 4% at the utmost so

we may assume that the maximum error involved in the assumption

$$\frac{d \log \eta / d\left(\frac{1}{T}\right)}{T_1} \Big/ \frac{d \log \eta / d\left(\frac{1}{T}\right)}{T_2} = \frac{M_1}{M_2}$$ will be about 4%.

The maximum and minimum possible values of the molecular association in the cases of methyl, ethyl, propyl and butyl alcohols as calculated by the author are given in Table III.

TABLE III.

Alcohols.	Maximum value of (x).	Minimum value of (x)
Methyl	1·9	1·1
Ethyl	2·4	1·6
Propyl	3·1	1·9
Butyl	3·1	1·9

If we accept the maximum value in the case of methyl alcohol, and minimum value in case of other alcohols, the molecular association seems to be least in the case of ethyl alcohol, whereas it should be least in the case of butyl alcohols. One explanation for this discrepancy might be that the assumptions of the author are less accurate than what he thinks. It might be also due to some error in the accepted values of the critical temperatures of the various alcohols as it seems rather surprising that the critical temperature of methyl and ethyl alcohols should be nearly the same. All the data have been taken from Bornstein-Landolt's tables.

SUMMARY.

1. The value of β for associated liquids corresponding to the unassociated state is calculated from the approximate relationship, $\beta/T_c = 0{\cdot}7$.

2. The molecular association (x) at any temperature is calculated from the formula, $x = \dfrac{d \log \eta / d\left(\frac{1}{T}\right)}{\beta}$.

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